Supporting Information

General rhodium-catalyzed oxidative cross-coupling reactions between anilines: synthesis of unsymmetrical 2,2'-diaminobiaryls

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I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26; DMSO-d_6: δ = 2.50). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16; DMSO-d_6: δ = 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. Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $RhCl_3•3H_2O$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. Pivaloyl chloride was purchased from Adamas-beta Ltd. Ag salts were purchased from Tianjin Yin Li Da Chemical Engineering (China) CO., Ltd. All *N*-phenylpivalamide **1**[1] and *N*-phenylacetamide **2**[2] were prepared according to the literature procedures. Solvents were dried with an innovative technology solvent purification system (model no.: PS-MD-5). All syntheses and manipulations were carried out under an N_2 atmosphere.

II. General procedure for the synthesis of *N*-phenylpivalamide derivatives[1]

A 100 mL two-necked round bottom flask was charged with aniline derivatives (20 mmol), CH_2Cl_2 (40 mL) and Et_3N (4.0 mL, 28 mmol). Then the reaction solution was cooled to 0 °C. Pivaloyl chloride (3.0 mL, 24 mmol) was added dropwise. After addition, the solution was stirred at room temperature for 10 h. Then the reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was dried and concentrated, and the resulting residue was purified by column chromatography on silica gel to provide *N*-phenylpivalamide derivatives.

III. General procedure for the synthesis of *N*-phenylacetamide derivatives[2]

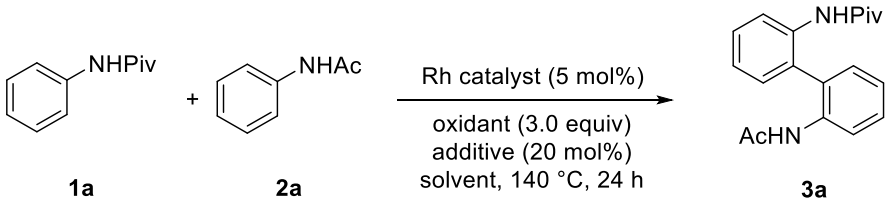
A 100 mL two-necked round bottom flask was charged with aniline derivatives (20 mmol), CH_2Cl_2 (40 mL) and Et_3N (4.0 mL, 28 mmol). Then the reaction solution was

cooled to 0 °C. Acetyl chloride (1.7 mL, 24 mmol) was added dropwise. After addition, the solution was stirred at room temperature for 10 h. Then the reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was dried and concentrated, and the resulting residue was purified by column chromatography on silica gel to provide *N*-phenylacetamide derivatives.

IV. Optimization of the rhodium-catalyzed oxidative C−H/C−H coupling between anilines

A Schlenk tube with a magnetic stir bar was charged with Rh catalyst (0.01 mmol, 5.0 mol%), oxidant (0.6 mmol, 3.0 equiv), *N*-phenylpivalamide **1a** (35.4 mg, 0.2 mmol, 1.0 equiv), *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol), additive (0.04 mmol, 20 mol%) and solvent (0.5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 140 °C for 24 h and then diluted with 3 mL of dichloromethane. The mixture 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 = 2/1, v/v) to provide **3a**.

Table S1. Optimization of the rhodium-catalyzed oxidative C−H/C−H coupling between **1a** and **2a**[a]



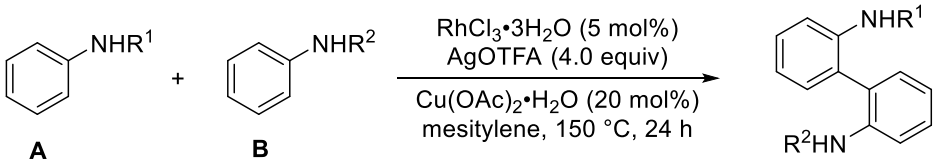
1a **2a** **3a**

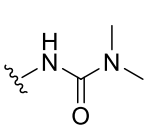
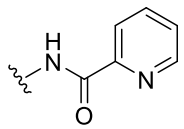
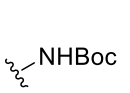
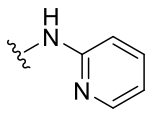
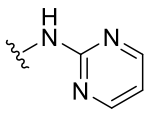
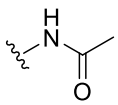
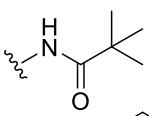
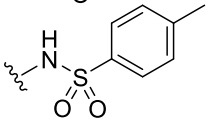
Entry	Catalyst	Oxidant	Additive	Solvent	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	AgOTFA	$Cu(OAc)_2•H_2O$	mesitylene	53
2	$[RhCp^*Cl_2]_2$	AgOTFA	$Cu(OAc)_2•H_2O$	1,4-dioxane	nd
3	$[RhCp^*Cl_2]_2$	AgOTFA	$Cu(OAc)_2•H_2O$	DCE	nd
4	$[RhCp^*Cl_2]_2$	AgOTFA	$Cu(OAc)_2•H_2O$	THF	nd
5[c]	$[RhCp^*Cl_2]_2$	AgOTFA	$Cu(OAc)_2•H_2O$	HFIP	45
6	$[RhCp^*Cl_2]_2$	AgOTFA	$Cu(OAc)_2•H_2O$	DMF	trace
7	$[RhCp^*Cl_2]_2$	Ag_2O	$Cu(OAc)_2•H_2O$	mesitylene	nr
8	$[RhCp^*Cl_2]_2$	Ag_2CO_3	$Cu(OAc)_2•H_2O$	mesitylene	nd
9	$[RhCp^*Cl_2]_2$	AgOAc	$Cu(OAc)_2•H_2O$	mesitylene	trace

10	$[RhCp^*Cl_2]_2$	$AgNO_3$	$Cu(OAc)_2•H_2O$	mesitylene	nr
11	$[RhCp^*Cl_2]_2$	AgOPiv	$Cu(OAc)_2•H_2O$	mesitylene	trace
12	$[RhCp^*Cl_2]_2$	$K_2S_2O_8$	$Cu(OAc)_2•H_2O$	mesitylene	nr
13	$[RhCp^*Cl_2]_2$	O_2	$Cu(OAc)_2•H_2O$	mesitylene	nr
14	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2•H_2O$	-	mesitylene	nr
15	$[RhCp^*Cl_2]_2$	$Cu(OTFA)_2•xH_2O$	-	mesitylene	nr
16	$RhCl_3•3H_2O$	AgOTFA	$Cu(OAc)_2•H_2O$	mesitylene	60
17	$RhCl_3•3H_2O$	Ag_2CO_3	$Cu(OTFA)_2•xH_2O$	mesitylene	nd
18[d]	$RhCl_3•3H_2O$	Ag_2CO_3	$Cu(OTFA)_2•xH_2O$	mesitylene	20
19	$RhCl_3•3H_2O$	AgOTFA	-	mesitylene	12
20	$RhCl_3•3H_2O$	AgOTFA	CuF_2	mesitylene	35
21	$RhCl_3•3H_2O$	AgOTFA	$Cu(OTf)_2$	mesitylene	42
22	$RhCl_3•3H_2O$	AgOTFA	$Cu(BF_4)(MeCN)_2$	mesitylene	23
23	$RhCl3•3H_2O$	AgOTFA	CuI	mesitylene	58
24	$RhCl_3•3H_2O$	AgOTFA	$Cu(acac)_2$	mesitylene	trace
25	$RhCl_3•3H_2O$	AgOTFA	$Cu(OTFA)_2•xH_2O$	mesitylene	70
26	$RhCl_3•3H_2O$	AgOTFA	$Cu(OTFA)_2•xH_2O$	mesitylene/HFIP	71
27[e]	$RhCl_3•3H_2O$	AgOTFA	$Cu(OTFA)_2•xH_2O$	mesitylene	78
28[e,f]	$RhCl_3•3H_2O$	AgOTFA	$Cu(OTFA)_2•xH_2O$	mesitylene	67

[a]Reaction conditions: *N*-phenylpivalamide **1a** (0.2 mmol), *N*-phenylacetamide **2a** (0.2 mmol), oxidant (3.0 equiv), additive (20 mol%), and solvent (0.5 mL) at 140 °C under an N_2 atmosphere for 24 h. [b]Yields of isolated products. [c]The reaction was carried out at 130 °C. [d]4.0 equiv trifluoroacetic acid was used. [e]1.2 equiv of *N*-phenylpivalamide **1a** was used. [f]The reaction was carried out for 12 h. nd (not detected) and nr (no reaction) were confirmed by the GC-MS analysis.

Table S2. Screening of the directing groups[a]



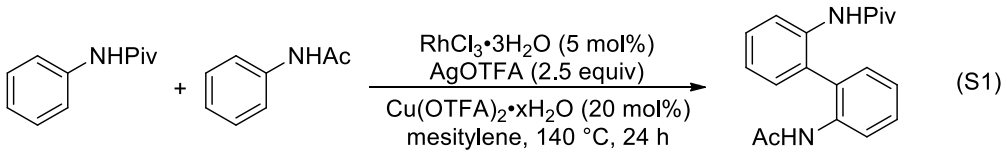
R1 \ R2					
	N.D.	N.D.	N.D.	N.D.	trace
	N.D.	N.D.	N.D.	trace	trace
	N.D.	N.D.	N.D.	N.D.	N.D.

[a] Reaction conditions: **A** (0.2 mmol, 1.0 equiv), **B** (0.2 mmol, 1.0 equiv), $RhCl_3 \cdot 3H_2O$ (5.0 mol %), AgOTFA (3.0 equiv), and $Cu(OAc)_2 \cdot H_2O$ (20 mol %) in mesitylene (0.5 mL) at 140 °C for 24 h under an N_2 atmosphere.

V. General procedure for the rhodium-catalyzed oxidative C−H/C−H coupling between *N*-phenylpivalamide derivatives and *N*-phenylacetamide derivatives.

A Schlenk tube with a magnetic stir bar was charged with $RhCl_3 \cdot 3H_2O$ (2.6 mg, 0.01 mmol, 5.0 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2 \cdot xH_2O$ (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylpivalamide derivative **1** (0.24 mmol, 1.2 equiv), *N*-phenylacetamide derivative **2** (0.2 mmol) and mesitylene (0.5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 140 °C for 24 h and then diluted with 3 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 product.

VI. Gram-scale synthesis of 3a.

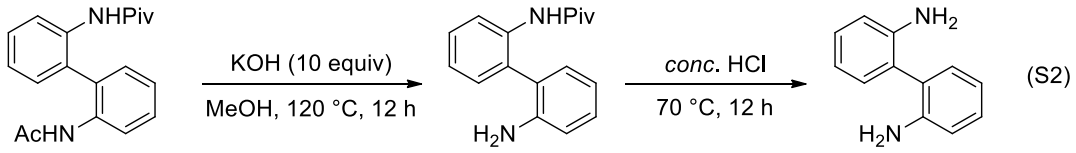


(S1)

1a (7.2 mmol) **2a** (6.0 mmol) **3a**, 69% (1.28 g)

A 50 mL two-necked round bottom flask with a magnetic stir bar was charged with $RhCl_3 \cdot 3H_2O$ (79.0 mg, 0.3 mmol, 5.0 mol%), AgOTFA (3.31 g, 15.0 mmol, 2.5 equiv), $Cu(OTFA)_2 \cdot xH_2O$ (347.5 mg, 1.2 mmol, 20.0 mol%), *N*-phenylpivalamide **1a** (1.27 g, 7.2 mmol, 1.2 equiv), *N*-phenylacetamide **2a** (811.0 mg, 6.0 mmol) and mesitylene (5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 140 °C for 24 h and then diluted with 15 mL of dichloromethane. The solution was filtered through a celite pad and washed with 60 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) to provide **3a** as a white solid in 69% yield (1.28g).

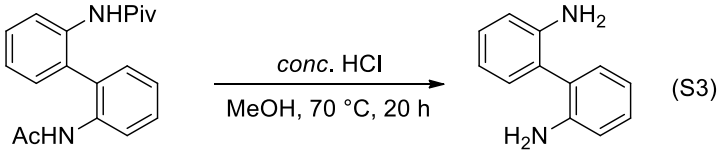
VII. Removal of the directing groups of 3a.



3a **5a** **6a** (S2)

A Schlenk tube with a magnetic stir bar was charged with *N*-(2'-acetamido-[1,1'-biphenyl]-2-yl)pivalamide **3a** (62.1 mg, 0.2 mmol), KOH (112.2 mg), and MeOH (1 mL). The resulting mixture was stirred at 120 °C for 12 h and then diluted with 3 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 = 3/2, v/v) to provide *N*-(2'-amino-[1,1'-biphenyl]-2-yl)pivalamide **5a** as a light yellow solid in 87% yield (49.8 mg).

A Schlenk tube with a magnetic stir bar was charged with *N*-(2'-amino-[1,1'-biphenyl]-2-yl)pivalamide **5a** (57.3 mg, 0.2 mmol) and *conc*. HCl (1 mL). The resulting mixture was stirred at 70 °C for 12 h. Then the mixture was quenched with water, neutralized with K_2CO_3, and extracted with dichloromethane. The organic layer was dried and concentrated, and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to provide [1,1'-biphenyl]-2,2'-diamine **6a** as a white solid in 93% yield (34.3 mg).



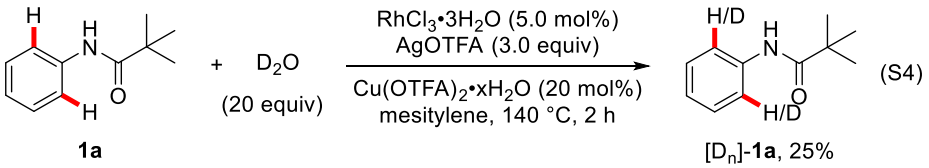
3a **6a** (S3)

A Schlenk tube with a magnetic stir bar was charged with *N*-(2'-acetamido-[1,1'-biphenyl]-2-yl)pivalamide **3a** (62.1 mg, 0.2 mmol), *conc*. HCl (1 mL), and MeOH (1 mL). The resulting mixture was stirred at 70 °C for 12 h. Then the mixture was quenched with water, neutralized with K_2CO_3, and extracted with dichloromethane. The organic layer was dried and concentrated, and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to provide [1,1'-biphenyl]-2,2'-diamine **6a** as a white solid in 88% yield

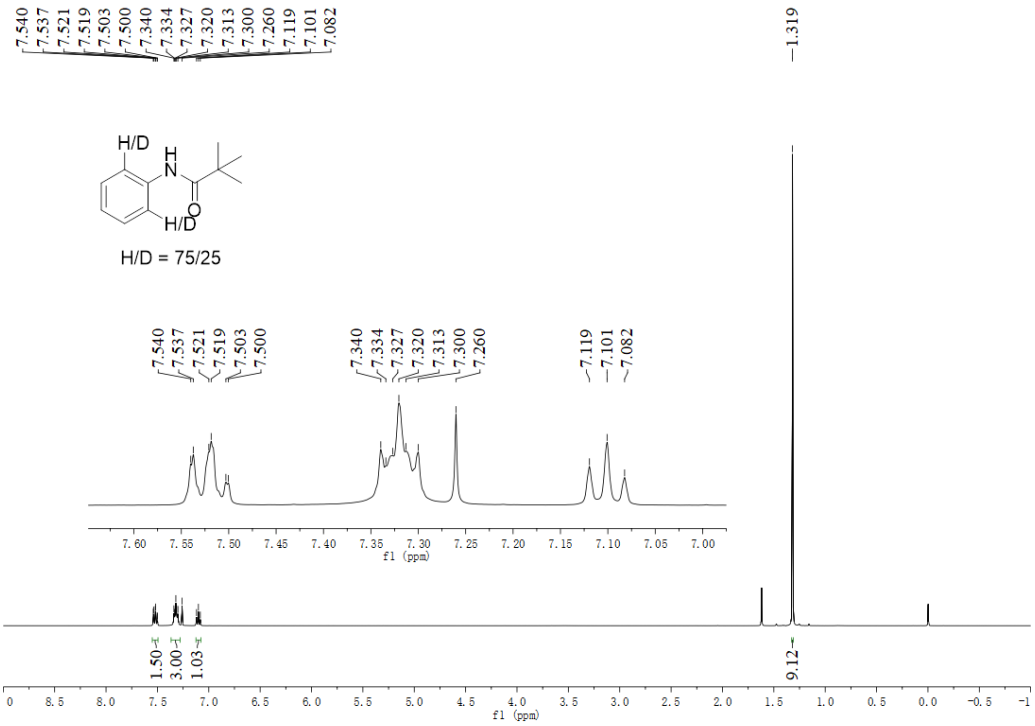
(32.4 mg).

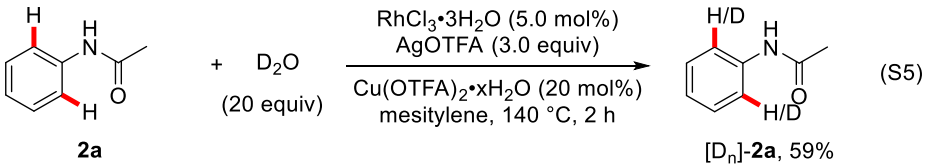
VIII. Mechanistic study.

1. H/D exchange experiments.

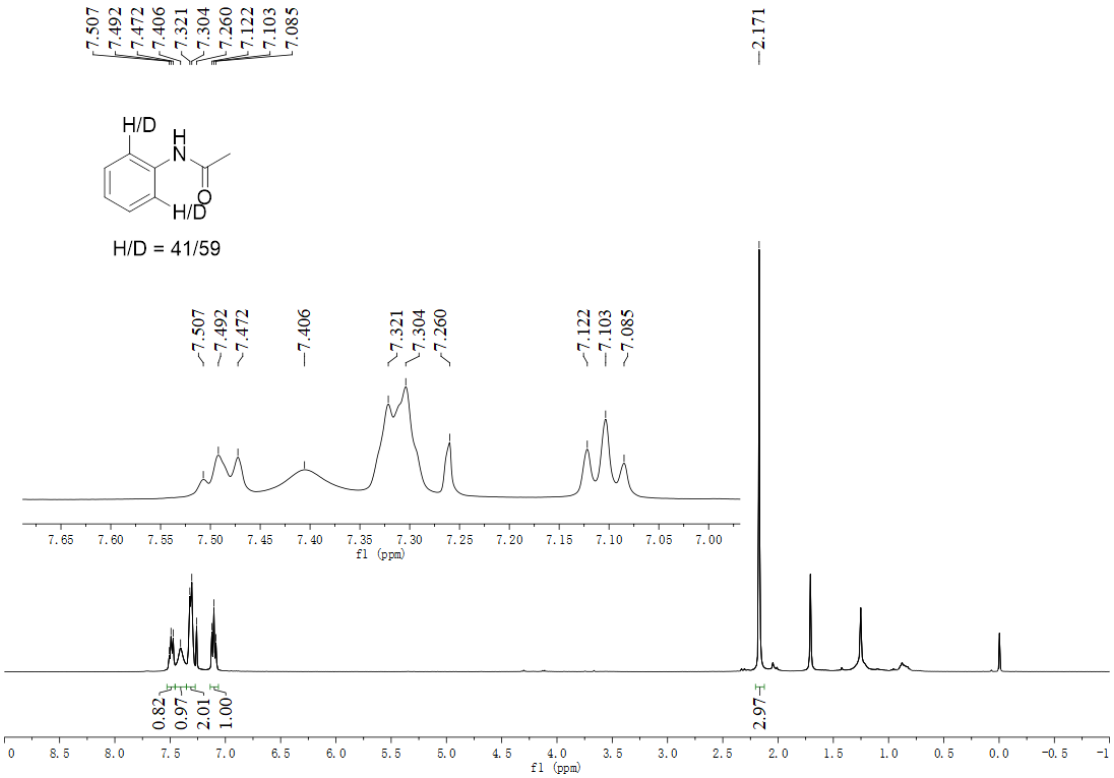


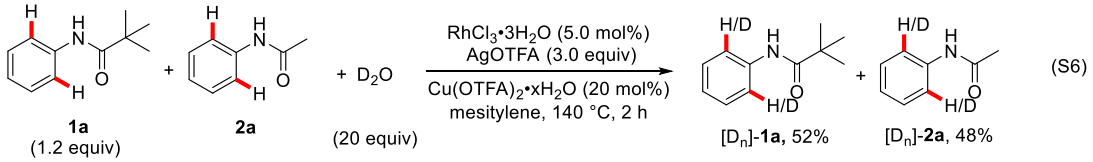
A Schlenk tube with a magnetic stir bar was charged with $RhCl_3•3H_2O$ (2.6 mg, 0.01 mmol, 5.0 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2•xH_2O$ (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylpivalamide **1a** (35.4 mg, 0.2 mmol), D_2O (72 μL, 4.0 mmol, 20.0 equiv), and mesitylene (0.5 mL) under an N_2 atmosphere and then heated at 140 °C in a pre-heated oil bath for 2 h. The mixture was cooled and then diluted with 3 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculated according to ^1H NMR analysis.



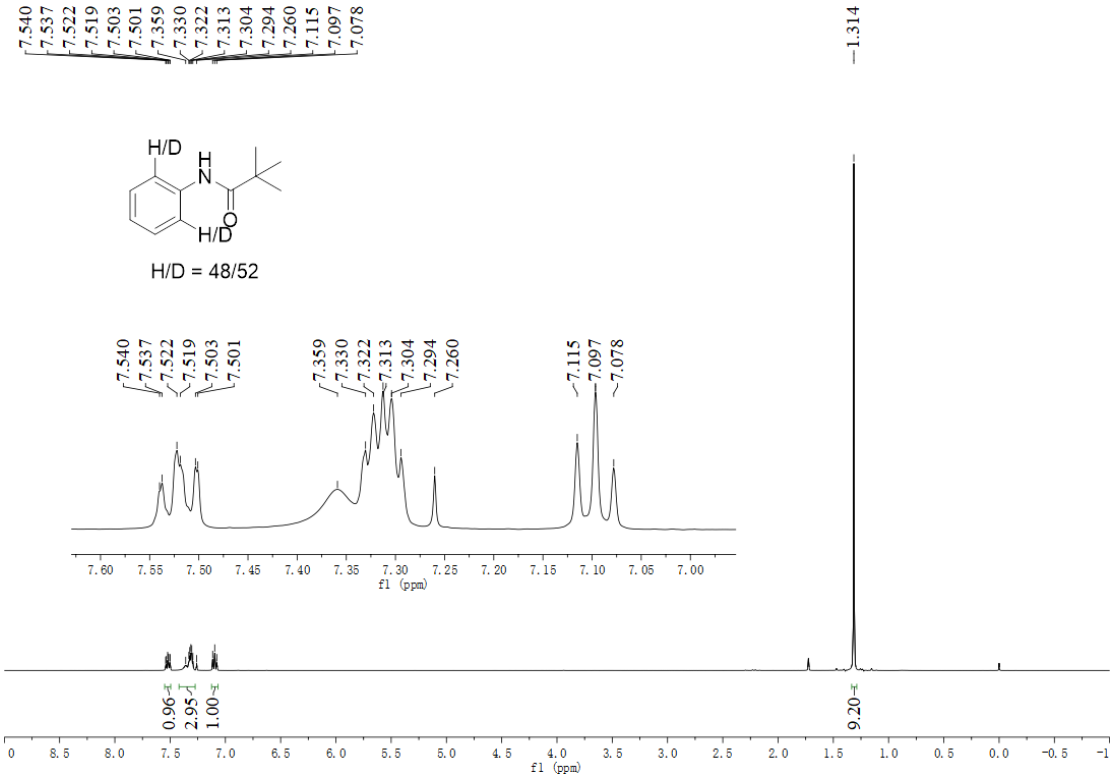


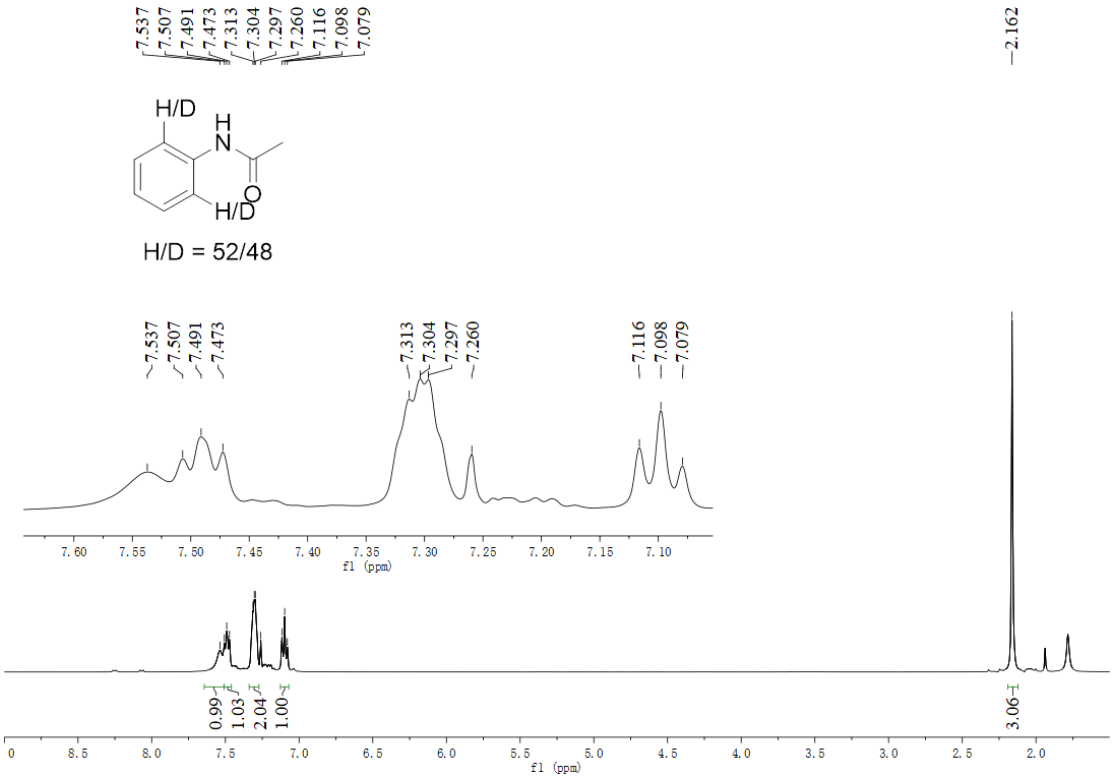
A Schlenk tube with a magnetic stir bar was charged with $RhCl_3•3H_2O$ (2.6 mg, 0.01 mmol, 5.0 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2•xH_2O$ (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol), D_2O (72 μL, 4.0 mmol, 20.0 equiv), and mesitylene (0.5 mL) under an N_2 atmosphere and then heated at 140 °C in a pre-heated oil bath for 2 h. The mixture was cooled and then diluted with 3 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculated according to ^1H NMR analysis.





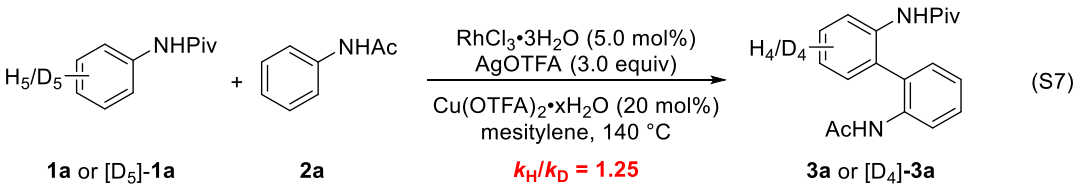
A Schlenk tube with a magnetic stir bar was charged with $RhCl_3$•$3H_2O$ (2.6 mg, 0.01 mmol, 5.0 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2$•xH_2O (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol, 1.2 equiv), *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol), D_2O (72 μL, 4.0 mmol, 20.0 equiv), and mesitylene (0.5 mL) under an N_2 atmosphere and then heated at 140 °C in a pre-heated oil bath for 2 h. The mixture was cooled and then diluted with 3 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculated according to ^1H NMR analysis.





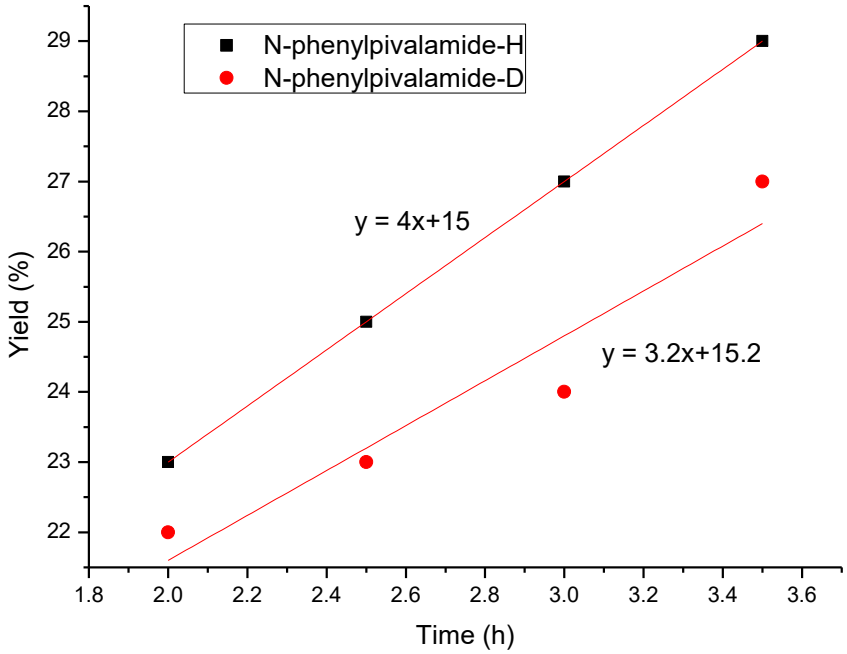
2. Kinetic isotope experiments.

A Schlenk tube with a magnetic stir bar was charged with $RhCl_3•3H_2O$ (2.6 mg, 0.01 mmol, 5.0 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2•xH_2O$ (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol, 1.2 equiv) or [D_5]-**1a** (43.7 mg, 0.24 mol), *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) and mesitylene (0.5 mL) under an N_2 atmosphere and then heated at 140 °C in a pre-heated oil bath for the indicated time. The reaction mixture was cooled to room temperature and diluted with 3 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The yield of **3a** or [D_4]-**3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.1 mmol, 7 μL) as internal standard. The KIE value was found to be 1.25.

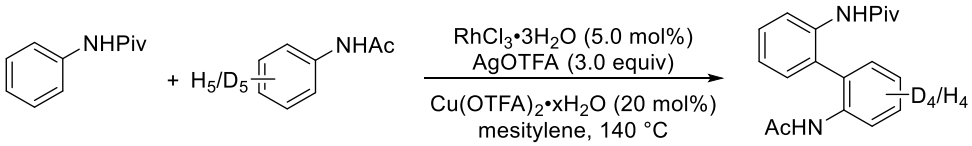


(S7)

Entry	Time (h)	Yield of **3a** (%)	Yield of [D_4]-**3a** (%)
1	2	23	22
2	2.5	25	23
3	3	27	24
4	3.5	29	27



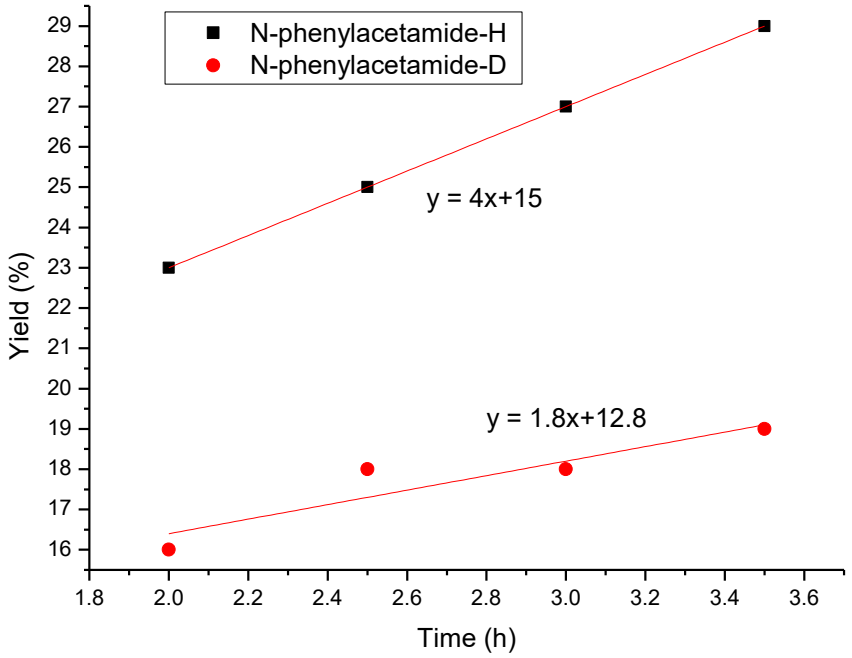
A Schlenk tube with a magnetic stir bar was charged with $RhCl_3$•$3H_2O$ (2.6 mg, 0.01 mmol, 5.0 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2$•xH_2O (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol, 1.2 equiv), *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) or [D_5]-**2a** (28.0 mg, 0.2 mol) and mesitylene (0.5 mL) under an N_2 atmosphere and then heated at 140 °C in a pre-heated oil bath for the indicated time. The reaction mixture was cooled to room temperature and diluted with 3 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The yield of **3a** or [D_4]-**3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.1 mmol, 7 μL) as internal standard. The KIE value was found to be 2.22



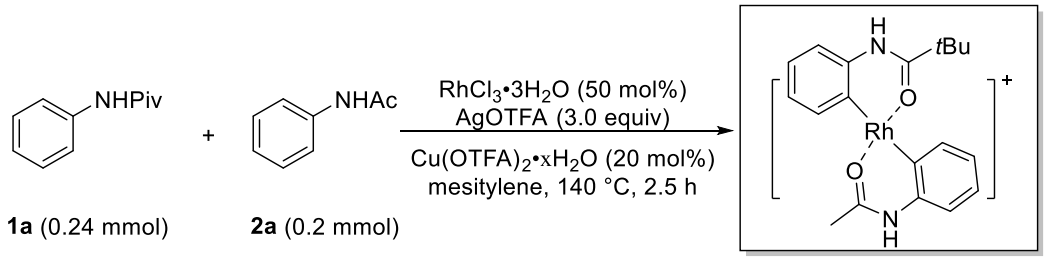
(S8)

1a **2a** or [D_5]-**2a** k_H/k_D = 2.22 **3a** or [D_4]-**3a**

Entry	Time (h)	Yield of **3a** (%)	Yield of [D_4]-**3a** (%)
1	2	23	16
2	2.5	25	18
3	3	27	18
4	3.5	29	19

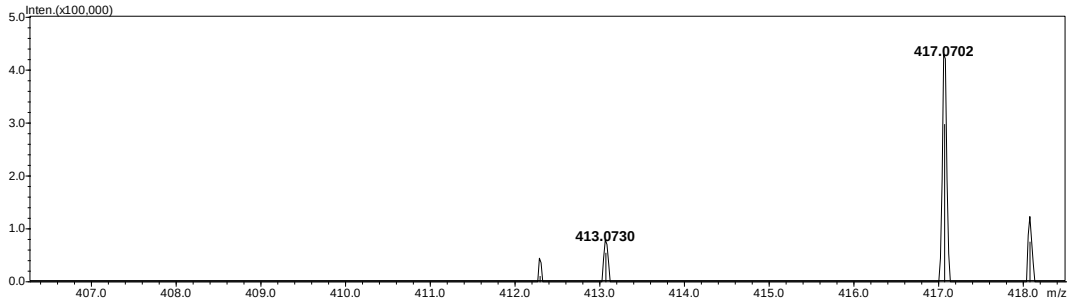


3. ESI-HRMS analysis.



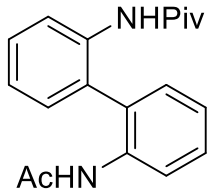
(S9)

1a (0.24 mmol) **2a** (0.2 mmol)



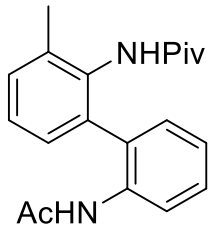
A Schlenk tube with a magnetic stir bar was charged with $RhCl_3$•$3H_2O$ (26.2 mg, 0.05mmol, 25 mol%), AgOTFA (131.9 mg, 0.6 mmol, 3.0 equiv), $Cu(OTFA)_2$•xH_2O (11.9 mg, 0.04 mmol, 20 mol%), *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol, 1.2 equiv), *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) and mesitylene (0.5 mL) under an N_2 atmosphere and then heated at 140 °C in a pre-heated oil bath for 2.5 h. The reaction mixture was cooled to room temperature and detected by ESI-HRMS. HRMS (ESI): calcd for $[RhAr^1Ar^2]^+$ (Ar^1 = PhNHPiv, Ar^2 = PhNHAc): $C_{19}H_{22}N_2O_2Rh$ $[M]^+$ 413.0736, found 413.0730.

IX. Experimental data for the described substances.



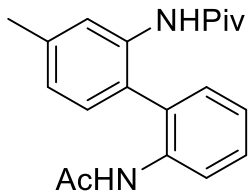
***N*-(2'-Acetamido-[1,1'-biphenyl]-2-yl)pivalamide (3a)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3a** as a white solid (48 mg, 78% yield). M.p.: 80-81 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.94 (s, 9H), 1.78 (s, 3H), 7.07-7.12 (m, 2H), 7.22-7.26 (m, 2H), 7.36-7.40 (m, 2H), 7.55-7.60 (m, 2H), 8.30 (bs, 1H), 8.88 (bs, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.0, 26.9, 38.6, 125.1, 125.4, 125.56, 125.59, 128.0, 128.3, 129.9, 130.5, 133.90, 133.91, 135.8, 135.9, 169.0, 176.3 ppm. HRMS (ESI): calcd for $C_{19}H_{23}N_2O_2$ $[M+H]^+$ 311.1754, found 311.1757.



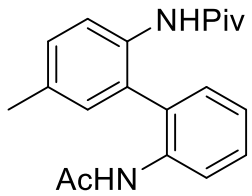
***N*-(2'-Acetamido-3-methyl-[1,1'-biphenyl]-2-yl)pivalamide (3b)**

Following the general procedure, *N*-(*o*-tolyl)pivalamide **1b** (45.9 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3b** as a white solid (29 mg, 45% yield). M.p.: 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.94 (s, 3H), 2.26 (s, 3H), 6.84 (bs, 1H), 7.06-7.15 (m, 3H), 7.27-7.37 (m, 4H), 8.17 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 24.5, 27.4, 39.2, 110.2, 122.3, 124.2, 127.9, 128.3, 128.8, 129.8, 131.0, 133.8, 136.2, 137.1, 169.4, 178.1 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_2Na$ $[M+Na]^+$ 347.1730, found 347.1729.



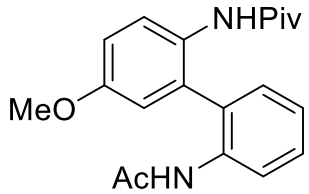
***N*-(2'-Acetamido-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide (3c)**

Following the general procedure, *N*-(*m*-Tolyl)pivalamide **1c** (45.9 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3c** as a white solid (54 mg, 83% yield). M.p.: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.95 (s, 3H), 2.42 (s, 3H), 6.97 (bs, 1H), 7.05-7.07 (m 1H), 7.10-7.12 (m, 2H), 7.16-7.22 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.98 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 24.7, 27.3, 39.7, 121.7, 123.7, 124.6, 126.1, 127.7, 129.5, 130.1, 130.4, 135.5, 136.1, 139.8, 168.7, 177.3 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_2Na$ $[M+Na]^+$ 347.1730, found 347.1728.



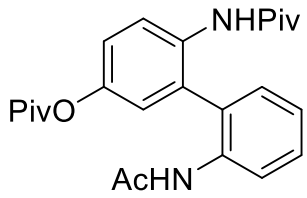
***N*-(2'-Acetamido-5-methyl-[1,1'-biphenyl]-2-yl)pivalamide (3d)**

Following the general procedure, *N*-(*p*-tolyl)pivalamide **1d** (45.9 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3d** as a white solid (52 mg, 80% yield). M.p.: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.95 (s, 3H), 2.37 (s, 3H), 7.02-7.04 (m, 3H), 7.15-7.22 (m, 2H), 7.24-7.26 (overlap, 1H), 7.39-7.43 (m, 1H), 7.90 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 24.7, 27.3, 39.6, 121.8, 123.8, 124.6, 128.1, 129.4, 129.8, 130.19, 130.21, 130.9, 133.0, 135.4, 135.9, 168.8, 177.4 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_2Na$ $[M+Na]^+$ 347.1730, found 347.1727.



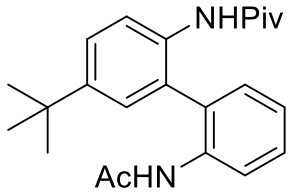
***N*-(2'-Acetamido-5-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (3e)**

Following the general procedure, *N*-(4-methoxyphenyl)pivalamide **1e** (49.7 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3e** as a white solid (43 mg, 64% yield). M.p.: 66-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.96 (s, 3H), 3.82 (s, 3H), 6.77 (d, J = 2.8 Hz, 1H), 6.95-7.00 (m, 2H), 7.10 (bs, 1H), 7.15-7.21 (m, 2H), 7.39-7.43 (m, 1H), 7.78 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.3, 39.4, 55.7, 110.1, 114.9, 115.4, 122.0, 124.6, 126.4, 128.4, 129.4, 130.0, 132.5, 135.9, 157.4, 169.0, 177.8 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$ 363.1679, found 363.1681.



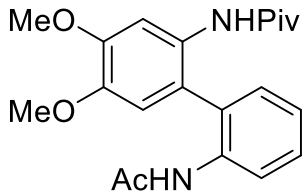
2'-Acetamido-6-pivalamido-[1,1'-biphenyl]-3-yl pivalate (3f)

Following the general procedure, 4-pivalamidophenyl pivalate **1f** (66.6 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3f** as a white solid (55 mg, 67% yield). M.p.: 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.34 (s, 9H), 1.99 (s, 3H), 6.96 (d, J = 2.8 Hz, 1H), 7.08 (bs, 1H), 7.13 (dd, J = 8.8 Hz, 2.8 Hz, 1H), 7.18 (bs, 1H), 7.21 (d, J = 4.4 Hz, 2H), 7.41-7.46 (m, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.26, 27.31, 39.2, 39.7, 122.4, 122.5, 123.6, 124.4, 124.8, 127.3, 129.8, 130.1, 130.4, 133.3, 135.9, 147.8, 169.1, 177.3 ppm. HRMS (ESI): calcd for $C_{24}H_{30}N_2O_4Na$ $[M+Na]^+$ 433.2098, found 433.2094.



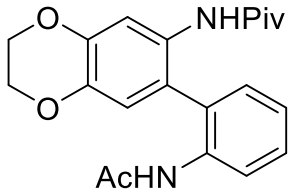
***N*-(2'-Acetamido-5-(*tert*-butyl)-[1,1'-biphenyl]-2-yl)pivalamide (3g)**

Following the general procedure, *N*-(4-(*tert*-butyl)phenyl)pivalamide **1g** (56.0 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3g** as a white solid (62 mg, 85% yield). M.p.: 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.33 (s, 9H), 1.95 (s, 3H), 7.03 (bs, 1H), 7.10 (bs, 1H), 7.20-7.23 (m, 3H), 7.40-7.48 (m, 2H), 7.96 (d, J = 8.8 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 27.3, 31.5, 34.7, 39.6, 121.9, 123.3, 124.6, 126.6, 127.3, 128.4, 129.2, 129.4, 130.3, 132.9, 135.9, 148.6, 168.8, 177.4 ppm. HRMS (ESI): calcd for $C_{23}H_{30}N_2O_2Na$ $[M+Na]^+$ 389.2199, found 389.2196.



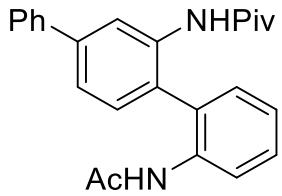
***N*-(2'-Acetamido-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)pivalamide (3h)**

Following the general procedure, *N*-(3,4-dimethoxyphenyl)pivalamide **1h** (57.0 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 1/1, v/v) afforded **3h** as a white solid (53 mg, 72% yield). M.p.: 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.97 (s, 3H), 3.86 (s, 3H), 3.96 (s, 3H), 6.70 (s, 1H), 7.04 (d, *J* = 6.8 Hz, 2H), 7.19-7.22 (m, 2H), 7.40-7.44 (m, 1H), 7.71 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 27.3, 39.6, 56.2, 56.3, 107.3, 112.5, 121.1, 121.7, 124.6, 127.6, 129.0, 129.5, 130.5, 136.2, 146.5, 149.3, 168.8, 177.4 ppm. HRMS (ESI): calcd for $C_{21}H_{26}N_2O_4Na$ $[M+Na]^+$ 393.1785, found 393.1778.



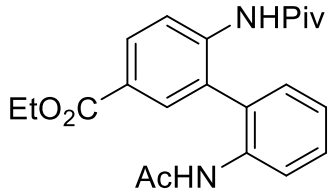
***N*-(7-(2-Acetamidophenyl)-2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)pivalamide (3i)**

Following the general procedure, *N*-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)pivalamide **1i** (56.5 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3i** as a white solid (63 mg, 86% yield). M.p.: 78-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 9H), 1.98 (s, 3H), 4.25-4.31 (m, 4H), 6.72 (s, 1H), 6.96 (bs, 1H), 7.10-7.18 (m, 3H), 7.36-7.40 (m, 1H), 7.53 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 27.3, 39.5, 64.46, 64.48, 113.3, 118.4, 121.7, 123.3, 124.5, 127.5, 129.0, 129.3, 130.5, 136.2, 141.2, 144.0, 168.8, 177.3 ppm. HRMS (ESI): calcd for $C_{21}H_{24}N_2O_4Na$ $[M+Na]^+$ 391.1628, found 391.1628.



***N*-(2-Acetamido-[1,1':4',1''-terphenyl]-2'-yl)pivalamide (3j)**

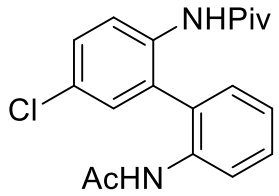
Following the general procedure, *N*-([1,1'-biphenyl]-3-yl)pivalamide **1j** (60.8 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3j** as a white solid (55 mg, 71% yield). M.p.: 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 (s, 9H), 2.00 (s, 3H), 6.79 (bs, 1H), 7.07-7.08 (m, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.25-7.27 (overlap, 1H), 7.32-7.44 (m, 8H), 7.66 (bs, 1H), 7.97 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 27.0, 38.8, 124.1, 124.4, 127.6, 127.9, 128.3, 128.6, 129.0, 129.7, 130.1, 130.4, 132.0, 132.5, 136.1, 138.0, 139.1, 141.1, 169.4, 178.3 ppm. HRMS (ESI): calcd for $C_{25}H_{26}N_2O_2Na$ $[M+Na]^+$ 409.1886, found 409.1886.



Ethyl 2'-acetamido-6-pivalamido-[1,1'-biphenyl]-3-carboxylate (3k)

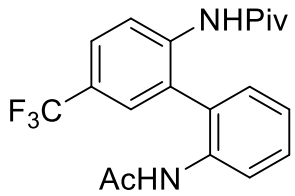
Following the general procedure, ethyl 4-pivalamidobenzoate **1k** (59.8 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3k** as a white solid (49 mg, 64% yield). M.p.: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.94 (s, 3H), 4.37 (q, *J* = 7.2 Hz, 2H), 6.81 (bs, 1H), 7.20-7.23 (m, 1H), 7.26-7.30 (overlap, 1H), 7.38 (bs, 1H), 7.46-7.51 (m, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 8.12 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 24.5, 27.2, 40.0, 61.3, 110.2, 121.3, 122.8, 125.4, 126.4, 127.9, 130.1, 130.5, 131.2, 131.5, 135.7, 140.1, 166.0, 168.7, 177.3 ppm. HRMS (ESI): calcd for $C_{22}H_{26}N_2O_4Na$ $[M+Na]^+$

405.1785, found 405.1779.



***N*-(2'-Acetamido-5-chloro-[1,1'-biphenyl]-2-yl)pivalamide (3l)**

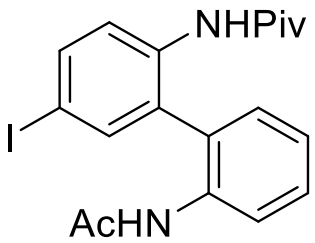
Following the general procedure, *N*-(4-chlorophenyl)pivalamide **1l** (50.8 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3l** as a white solid (41 mg, 60% yield). M.p.: 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.97 (s, 3H), 6.93 (bs, 1H), 7.16-7.24 (m, 4H), 7.39-7.47 (m, 2H), 8.05 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 27.2, 39.7, 122.8, 124.7, 125.2, 127.5, 129.5, 130.01, 130.05, 130.2, 130.3, 131.2, 134.4, 135.6, 168.9, 177.4 ppm. HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2{}^{35}ClNa$ $[M+Na]^+$, 367.1184, found 367.1184 and $C_{19}H_{21}N_2O_2{}^{37}ClNa$ $[M+Na]^+$, 369.1154, found 369.1147.



***N*-(2'-Acetamido-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamide (3m)**

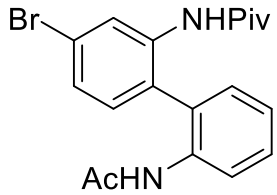
Following the general procedure, *N*-(4-(trifluoromethyl)phenyl)pivalamide **1m** (58.8 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3m** as a white solid (38 mg, 50% yield). M.p.: 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.96 (s, 3H), 6.80 (bs, 1H), 7.20-7.22 (m, 1H), 7.29-7.30 (m, 1H), 7.39 (bs, 1H), 7.48-7.51 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 27.2, 40.0, 122.4, 123.3, 124.0 (q, J = 271 Hz), 125.6, 126.7 (q, J = 4 Hz), 126.6 (q, J

= 33 Hz), 127.2 (q, *J* = 4 Hz), 127.5, 129.0, 130.3, 130.4, 135.6, 139.13 (q, *J* = 1 Hz), 168.9, 177.4 ppm. HRMS (ESI): calcd for $C_{20}H_{22}N_2O_2F_3$ $[M+H]^+$, 379.1628, found 379.1631.



***N*-(2'-Acetamido-5-iodo-[1,1'-biphenyl]-2-yl)pivalamide (3n)**

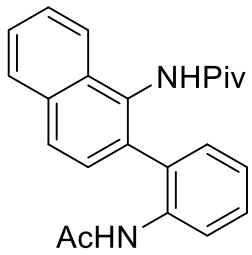
Following the general procedure, *N*-(4-iodophenyl)pivalamide **1n** (72.8 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 4/1, v/v) afforded **3n** as a white solid (37 mg, 42% yield). M.p.: 182-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.97 (s, 3H), 6.90 (bs, 1H), 7.16-7.18 (m, 2H), 7.22-7.24 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.72-7.75 (m, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 27.2, 39.8, 88.7, 122.8, 124.9, 125.2, 127.1, 130.0, 130.3, 131.5, 135.6, 135.7, 138.4, 138.7, 168.9, 177.4 ppm. HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2INa$ $[M+Na]^+$, 459.0540, found 459.0540.



***N*-(2'-Acetamido-4-bromo-[1,1'-biphenyl]-2-yl)pivalamide (3o)**

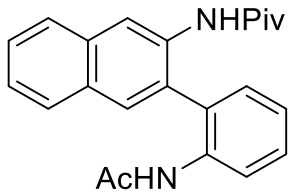
Following the general procedure, *N*-(3-bromophenyl)pivalamide **1o** (61.5 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3o** as a white solid (45 mg, 58% yield). M.p.: 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.97 (s, 3H), 6.87 (bs, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.2

Hz, 1H), 7.21-7.24 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.2, 39.8, 122.7, 123.4, 125.2, 125.7, 127.3, 127.6, 128.1, 130.0, 130.3, 131.4, 135.7, 137.1, 168.8, 177.3 ppm. HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2{}^{79}BrNa$ $[M+Na]^+$, 411.0679, found 411.0673 and $C_{19}H_{21}N_2O_2{}^{81}BrNa$ $[M+Na]^+$, 413.0658, found 413.0653.



***N*-(2-(2-Acetamidophenyl)naphthalen-1-yl)pivalamide (3p)**

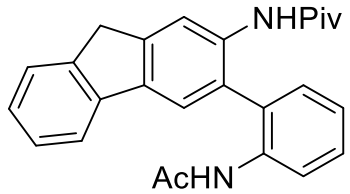
Following the general procedure, *N*-(naphthalen-1-yl)pivalamide **1p** (54.6 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3p** as a white solid (47 mg, 65% yield). M.p.: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 9H), 1.89 (s, 3H), 7.11-7.13 (m, 1H), 7.16-7.21 (m, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.37-7.42 (m, 1H), 7.49 (bs, 1H), 7.55-7.60 (m, 2H), 7.81-7.83 (m, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.92-7.94 (m, 1H), 8.12 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 27.5, 39.4, 123.1, 123.17, 123.19, 124.5, 126.8, 127.4, 127.7, 128.46, 128.51, 128.9, 129.8, 130.8, 131.1, 134.1, 134.2, 136.2, 169.5, 179.1 ppm. HRMS (ESI): calcd for $C_{23}H_{24}N_2O_2Na$ $[M+Na]^+$ 383.1730, found 383.1727.



***N*-(3-(2-Acetamidophenyl)naphthalen-2-yl)pivalamide (3q)**

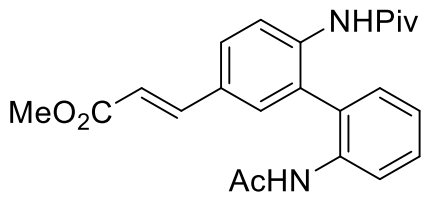
Following the general procedure, *N*-(naphthalen-2-yl)pivalamide **1q** (54.6 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3q**

as a white solid (50 mg, 70% yield). M.p.: 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9H), 1.90 (s, 3H), 6.91 (bs, 1H), 7.27-7.30 (m, 2H), 7.33 (bs, 1H), 7.46-7.56 (m, 3H), 7.73 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.77 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.3, 39.9, 119.5, 122.2, 124.9, 125.9, 127.2, 127.55, 127.64, 128.1, 128.6, 129.7, 129.9, 130.5, 130.6, 133.1, 134.1, 136.2, 168.7, 177.4 ppm. HRMS (ESI): calcd for $C_{23}H_{24}N_2O_2Na$ $[M+Na]^+$ 383.1730, found 383.1727.



***N*-(3-(2-Acetamidophenyl)-9*H*-fluoren-2-yl)pivalamide (3r)**

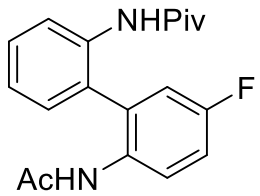
Following the general procedure, *N*-(9*H*-fluoren-2-yl)pivalamide **1r** (63.7 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3r** as a white solid (55 mg, 70% yield). M.p.: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9H), 1.93 (s, 3H), 3.99 (s, 2H), 7.01 (bs, 1H), 7.23-7.25 (m, 2H), 7.27-7.34 (m, 2H), 7.36-7.40 (m, 1H), 7.45-7.49 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.63 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 8.35-8.37 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 27.3, 37.2, 39.8, 119.80, 119.84, 121.4, 121.9, 124.8, 125.3, 127.0, 127.1, 127.8, 128.1, 129.7, 130.5, 134.4, 136.1, 138.9, 140.9, 143.6, 144.9, 168.8, 177.4 ppm. HRMS (ESI): calcd for $C_{26}H_{26}N_2O_2Na$ $[M+Na]^+$ 421.1886, found 421.1881.



Methyl (*E*)-3-(2'-acetamido-6-pivalamido-[1,1'-biphenyl]-3-yl)acrylate (3s)

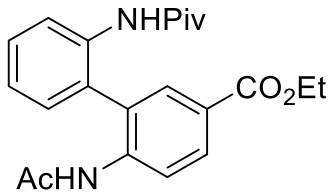
Following the general procedure, methyl (*E*)-3-(4-pivalamidophenyl)acrylate **1s** (62.7 mg, 0.24 mmol) and *N*-phenylacetamide **2a** (27.0 mg, 0.2 mmol) were used.

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3s** as a white solid (54 mg, 69% yield). M.p.: 73-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.95 (s, 3H), 3.79 (s, 3H), 6.40 (d, J = 16 Hz, 1H), 6.86 (bs, 1H), 7.19-7.21 (m, 1H), 7.24-7.28 (overlap, 2H), 7.38 (s, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 15.6 Hz, 1H), 8.25-8.30 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.2, 39.9, 51.9, 117.8, 122.6, 122.7, 125.2, 127.4, 129.0, 129.4, 129.9, 130.1, 130.4, 131.0, 135.8, 137.8, 143.7, 167.4, 168.7, 177.3 ppm. HRMS (ESI): calcd for $C_{23}H_{26}N_2O_4Na$ $[M+Na]^+$ 417.1785, found 417.1781.



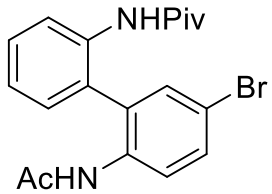
***N*-(2'-Acetamido-5'-fluoro-[1,1'-biphenyl]-2-yl)pivalamide (4a)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(4-fluorophenyl)acetamide **2b** (30.6 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 7/2, v/v) afforded **4a** as a white solid (41 mg, 62% yield). M.p.: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 9H), 1.93 (s, 3H), 6.91 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 6.98 (bs, 1H), 7.10-7.15 (m, 2H), 7.20-7.22 (m, 1H), 7.28-7.30 (m, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.14-8.18 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 27.3, 39.6, 116.0 (d, J = 22 Hz), 116.9 (d, J = 22 Hz), 124.5, 124.6 (d, J = 8 Hz), 125.9, 129.6, 129.9, 130.2, 131.0 (d, J = 8 Hz), 132.0 (d, J = 2 Hz), 135.4, 159.3 (d, J = 244 Hz), 169.0, 177.6 ppm. HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2FNa$ $[M+Na]^+$ 351.1479, found 351.1478.



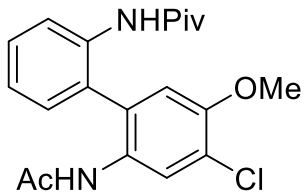
Ethyl 6-acetamido-2'-pivalamido-[1,1'-biphenyl]-3-carboxylate (4b)

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and ethyl 4-acetamidobenzoate **2c** (41.4 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 3/1, v/v) afforded **4b** as a white solid (54 mg, 70% yield). M.p.: 64-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.98 (s, 3H), 4.33-4.41 (m, 2H), 7.03 (bs, 1H), 7.17 (bs, 1H), 7.26-7.28 (overlap, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.48-7.52 (m, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.10 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 24.9, 27.3, 39.6, 61.3, 120.5, 124.8, 126.0, 126.2, 127.1, 129.4, 130.1, 130.7, 131.1, 131.7, 135.5, 140.1, 166.0, 169.0, 177.6 ppm. HRMS (ESI): calcd for $C_{22}H_{26}N_2O_4Na$ $[M+Na]^+$ 405.1785, found 405.1785.



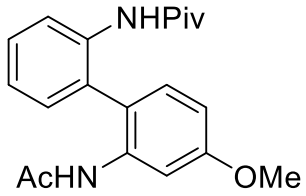
***N*-(2'-Acetamido-5'-bromo-[1,1'-biphenyl]-2-yl)pivalamide (4c)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(4-bromophenyl)acetamide **2d** (42.8 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 6/1, v/v) afforded **4c** as a white solid (41 mg, 66% yield). M.p.: 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 9H), 1.94 (s, 3H), 7.02 (bs, 1H), 7.09 (bs, 1H), 7.22 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.29 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.45-7.49 (m, 1H), 7.52 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.4, 39.7, 117.1, 123.6, 124.7, 126.0, 129.2, 130.1, 130.2, 130.4, 132.3, 132.9, 135.1, 135.4, 168.9, 177.6 ppm. HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2{}^{79}BrNa$ $[M+Na]^+$ 411.0679, found 411.0682 and $C_{19}H_{21}N_2O_2{}^{81}BrNa$ $[M+Na]^+$ 413.0658, found 413.0665.



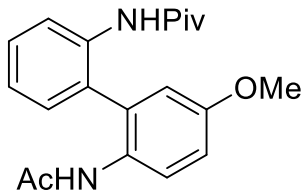
***N*-(2'-Acetamido-4'-chloro-5'-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (4d)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(3-chloro-4-methoxyphenyl)acetamide **2e** (39.9 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 4/1, v/v) afforded **4d** as a white solid (48 mg, 64% yield). M.p.: 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 9H), 1.91 (s, 3H), 3.85 (s, 3H), 6.73 (s, 1H), 6.91 (bs, 1H), 7.18-7.20 (m, 1H), 7.24-7.28 (m, 2H), 7.45 (t, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 8.20 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 27.4, 39.7, 56.6, 113.3, 122.9, 124.3, 125.2, 125.6, 129.1, 129.2, 129.7, 129.8, 130.2, 135.6, 152.2, 168.9, 177.6 ppm. HRMS (ESI): calcd for $C_{20}H_{23}N_2O_3{}^{35}ClNa$ $[M+Na]^+$ 397.1289, found 397.1287 and $C_{20}H_{23}N_2O_3{}^{37}ClNa$ $[M+Na]^+$ 399.1260, found 399.1264.



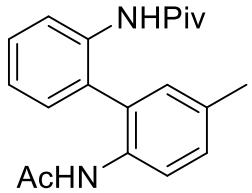
***N*-(2'-Acetamido-4'-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (4e)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(3-methoxyphenyl)acetamide **2f** (33.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 3/1, v/v) afforded **4e** as a white solid (56 mg, 83% yield). M.p.: 64-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 9H), 1.94 (s, 3H), 3.87 (s, 3H), 6.75-6.78 (m, 1H), 6.93 (bs, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.19-7.24 (m, 3H), 7.44 (t, J = 7.2 Hz, 1H), 8.06 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 27.4, 39.8, 55.6, 106.4, 110.9, 119.2, 123.0, 125.3, 128.6, 129.6, 130.9, 131.0, 136.1, 137.0, 160.4, 168.8, 177.3 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$ 363.1679, found 363.1673.



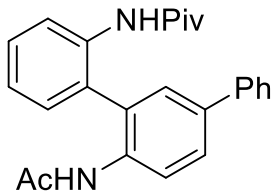
***N*-(2'-Acetamido-5'-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (4f)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(4-methoxyphenyl)acetamide **2g** (33.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 3/1, v/v) afforded **4f** as a white solid (50 mg, 74% yield). M.p.: 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9H), 1.90 (s, 3H), 3.79 (s, 3H), 6.72 (d, J = 2.4 Hz, 1H), 6.88 (bs, 1H), 6.96 (dd, J = 9.2 Hz, 2.8 Hz, 1H), 7.19-7.25 (m, 2H), 7.29 (bs, 1H), 7.43 (t, J = 7.2 Hz, 1H), 8.00-8.06 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 27.3, 39.7, 55.7, 114.7, 115.3, 123.6, 124.6, 125.3, 128.9, 129.5, 129.9, 130.1, 130.8, 135.2, 135.6, 156.7, 168.9 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$ 363.1679, found 363.1674.



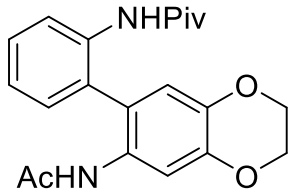
***N*-(2'-Acetamido-5'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (4g)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(*p*-tolyl)acetamide **2h** (29.8 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 3/1, v/v) afforded **4g** as a white solid (51 mg, 78% yield). M.p.: 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.92 (s, 3H), 2.35 (s, 3H), 6.90 (bs, 1H), 7.00 (s, 1H), 7.20-7.24 (m, 4H), 7.41-7.45 (m, 1H), 8.10-8.13 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 24.5, 27.3, 39.7, 122.3, 123.3, 125.2, 128.2, 129.0, 129.5, 130.1, 130.2, 130.8, 133.3, 134.6, 135.7, 168.8, 177.3 ppm. HRMS (ESI): calcd for $C_{20}H_{24}N_2O_2Na$ $[M+Na]^+$ 347.1730, found 347.1730.



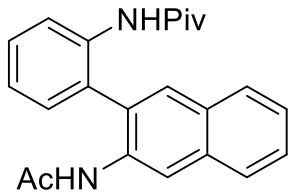
***N*-(6'-Acetamido-[1,1':3',1''-terphenyl]-2-yl)pivalamide (4h)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-([1,1'-biphenyl]-4-yl)acetamide **2i** (42.2 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 8/1, v/v) afforded **4h** as a white solid (56 mg, 73% yield). M.p.: 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.97 (s, 3H), 7.08 (bs, 1H), 7.24 (bs, 1H), 7.29-7.30 (m, 2H), 7.34-7.36 (m, 1H), 7.41-7.47 (m, 4H), 7.58-7.60 (m, 2H), 7.68 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.3, 39.7, 122.4, 123.8, 125.6, 126.8, 127.6, 128.0, 128.5, 128.7, 129.0, 129.7, 129.8, 130.4, 135.1, 135.7, 137.5, 139.8, 168.9, 177.5 ppm. HRMS (ESI): calcd for $C_{25}H_{27}N_2O_2$ $[M+H]^+$ 387.2067, found 387.2065.



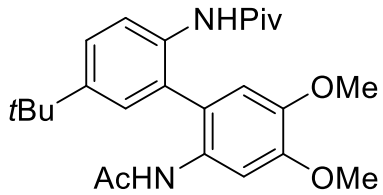
***N*-(2-(7-Acetamido-2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)phenyl)pivalamide (4i)**

Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)acetamide **2j** (38.6 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone/DCM = 6/2/1, v/v/v) afforded **4i** as a white solid (48 mg, 65% yield). M.p.: 166-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 9H), 1.90 (s, 3H), 4.26-4.31 (m, 4H), 6.70 (s, 1H), 6.80 (bs, 1H), 7.17-7.22 (m, 2H), 7.24-7.25 (m, 1H), 7.40-7.44 (m, 1H), 7.81 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 27.4, 39.8, 64.5, 64.6, 111.7, 118.4, 121.6, 123.3, 125.3, 129.0, 129.47, 129.48, 130.7, 135.9, 140.5, 143.8, 168.6, 177.4 ppm. HRMS (ESI): calcd for $C_{21}H_{24}N_2O_4Na$ $[M+Na]^+$ 391.1628, found 391.1628.



***N*-(2-(3-Acetamidonaphthalen-2-yl)phenyl)pivalamide (4j)**

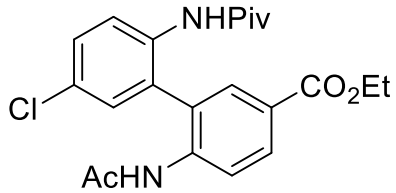
Following the general procedure, *N*-phenylpivalamide **1a** (42.5 mg, 0.24 mmol) and *N*-(naphthalen-2-yl)acetamide **2k** (37.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/acetone = 6/1, v/v) afforded **4j** as a white solid (59 mg, 82% yield). M.p.: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 9H), 1.99 (s, 3H), 7.09 (bs, 1H), 7.14 (bs, 1H), 7.29-7.34 (m, 2H), 7.44-7.48 (m, 1H), 7.49-7.54 (m, 2H), 7.70 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 27.3, 39.7, 118.4, 124.0, 125.7, 125.8, 127.1, 127.5, 127.9, 128.2, 129.3, 129.8, 129.9, 130.2, 130.9, 133.2, 134.0, 135.9, 169.0, 177.5 ppm. HRMS (ESI): calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$ 361.1911, found 361.1914.



***N*-(2'-Acetamido-5-(*tert*-butyl)-4',5'-dimethoxy-[1,1'-biphenyl]-2-yl)pivalamide (4k)**

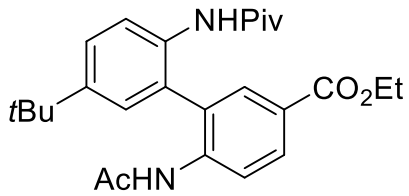
Following the general procedure, *N*-(4-(*tert*-Butyl)phenyl)pivalamide **1g** (56.0 mg, 0.24 mmol) and *N*-(3,4-dimethoxyphenyl)acetamide **2l** (39.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/ EtOAc = 4/1, v/v) afforded **4k** as a white solid (70 mg, 82% yield). M.p.: 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 9H), 1.33 (s, 9H), 1.94 (s, 3H), 3.86 (s, 3H), 3.96 (s, 3H), 6.69 (s, 1H), 6.91 (bs, 1H), 7.21 (d, *J* = 2.4 Hz, 2H), 7.46 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.96 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.5, 31.5, 34.7, 39.7, 56.2, 56.3, 106.2, 112.6, 120.2, 122.9, 126.5, 127.5, 128.7,

129.5, 133.3, 145.8, 148.4, 149.1, 168.8, 177.3 ppm. HRMS (ESI): calcd for $C_{25}H_{34}N_2O_4Na$ $[M+Na]^+$ 449.2411, found 449.2411.



Ethyl 6-acetamido-5'-chloro-2'-pivalamido-[1,1'-biphenyl]-3-carboxylate (4l)

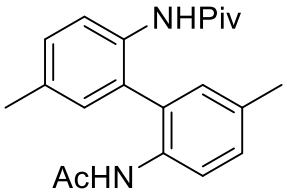
Following the general procedure, *N*-(4-chlorophenyl)pivalamide **1l** (50.8 mg, 0.24 mmol) and ethyl 4-acetamidobenzoate **2c** (41.4 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/ EtOAc = 4/1, v/v) afforded **4l** as a white solid (54 mg, 65% yield). M.p.: 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.39 (t, *J* = 7.2 Hz, 3H), 2.01 (s, 3H), 4.35-4.40 (m, 2H), 6.99 (bs, 1H), 7.08 (bs, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.46 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 8.11 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 24.8, 27.3, 39.7, 61.4, 120.9, 126.0, 126.1, 126.3, 130.1, 130.5, 131.0, 131.3, 131.5, 131.6, 134.1, 139.8, 165.8, 169.0, 177.7 ppm. HRMS (ESI): calcd for $C_{22}H_{25}{}^{35}ClN_2O_4Na$ $[M+Na]^+$ 439.1395, found 439.1395 and $C_{22}H_{25}{}^{37}ClN_2O_4Na$ $[M+Na]^+$ 441.1366, found 441.1365.



Ethyl 6-acetamido-5'-(*tert*-butyl)-2'-pivalamido-[1,1'-biphenyl]-3-carboxylate (4m)

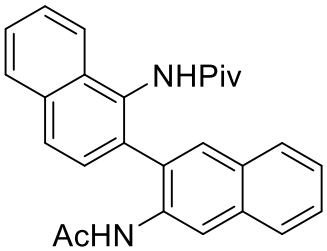
Following the general procedure, *N*-(4-(*tert*-butyl)phenyl)pivalamide **1g** (56.0 mg, 0.24 mmol) and ethyl 4-acetamidobenzoate **2c** (41.4 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/ EtOAc = 4/1, v/v) afforded **4m** as a white solid (70 mg, 80% yield). M.p.: 72-74 °C. ^{1}H NMR (400

MHz, $CDCl_3$): δ = 1.04 (s, 9H), 1.34 (s, 9H), 1.39 (t, J = 6.8 Hz, 3H), 1.99 (s, 3H), 4.36-4.39 (m, 2H), 6.98 (bs, 1H), 7.23-7.25 (m, 2H), 7.51 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 1.6 Hz, 1H), 8.09 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 24.9, 27.4, 31.5, 34.8, 39.5, 61.2, 120.4, 124.8, 125.8, 127.1, 127.5, 127.7, 129.2, 130.9, 131.7, 132.7, 140.2, 149.6, 166.1, 169.0, 177.7 ppm. HRMS (ESI): calcd for $C_{26}H_{34}N_2O_4Na$ $[M+Na]^+$ 461.2411, found 461.2410.



***N*-(2'-Acetamido-5,5'-dimethyl-[1,1'-biphenyl]-2-yl)pivalamide (4n)**

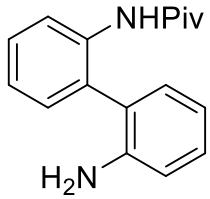
Following the general procedure, *N*-(*p*-tolyl)pivalamide **1d** (45.9 mg, 0.24 mmol) and *N*-(*p*-tolyl)acetamide **2h** (29.8 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/ EtOAc = 2/1, v/v) afforded **4n** as a white solid (49 mg, 72% yield). M.p.: 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.93 (s, 3H), 2.34 (s, 3H), 2.36 (s, 3H), 6.94 (bs, 1H), 6.98 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 2.0 Hz, 1H), 7.10 (bs, 1H), 7.20-7.25 (m, 2H), 7.90 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 21.0, 24.6, 27.3, 39.6, 121.9, 123.6, 128.2, 129.8, 129.9, 130.0, 130.7, 130.8, 133.0, 133.3, 134.3, 135.2, 168.8, 177.4 ppm. HRMS (ESI): calcd for $C_{21}H_{27}N_2O_4$ $[M+H]^+$ 339.2067, found 339.2068.



***N*-(3'-Acetamido-[2,2'-binaphthalen]-1-yl)pivalamide (4o)**

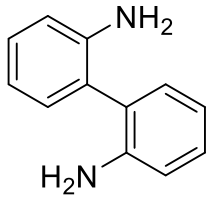
Following the general procedure, *N*-(*p*-tolyl)pivalamide **1p** (54.6 mg, 0.24 mmol) and

N-(*p*-tolyl)acetamide **2k** (37.0 mg, 0.2 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/ EtOAc = 2/1, v/v) afforded **4o** as a white solid (48 mg, 58% yield). M.p.: 190-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (s, 9H), 1.95 (s, 3H), 7.20 (bs, 1H), 7.42-7.46 (m, 2H), 7.48-7.52 (m, 1H), 7.56-7.61 (m, 3H), 7.62 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.80-7.83 (m, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.93-7.97 (m, 2H), 8.78 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 27.5, 39.4, 119.1, 123.4, 125.6, 126.8, 127.0, 127.4, 127.6, 128.0, 128.1, 128.57, 128.60, 129.1, 130.2, 130.5, 130.6, 131.5, 133.4, 133.7, 133.8, 134.2, 169.7, 179.1 ppm. HRMS (ESI): calcd for $C_{27}H_{26}N_2O_2Na$ $[M+Na]^+$ 433.1886, found 433.1886.



***N*-(2'-Amino-[1,1'-biphenyl]-2-yl)pivalamide (5a)**

A light yellow solid. M.p.: 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 9H), 3.65 (bs, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.86 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 7.07 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.15-7.20 (m, 1H), 7.20-7.24 (m, 1H), 7.24-7.26 (m, 1H), 7.36-7.40 (m, 1H), 7.83 (bs, 1H), 8.24 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.3, 39.7, 115.5, 119.2, 121.9, 123.4, 124.5, 128.8, 129.5, 130.4, 131.1, 136.0, 143.6, 176.8 ppm. HRMS (ESI): calcd for $C_{17}H_{20}N_2ONa$ $[M+Na]^+$ 291.1468, found 291.1472.



[1,1'-Biphenyl]-2,2'-diamine (6a)

A white solid. M.p.: 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (bs, 4H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.17-7.21 (m, 2H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.7, 118.9, 124.7, 128.9, 131.2, 144.2 ppm. HRMS (ESI): calcd for $C_{12}H_{13}N_2$ $[M+H]^+$ 185.1073, found 185.1077.

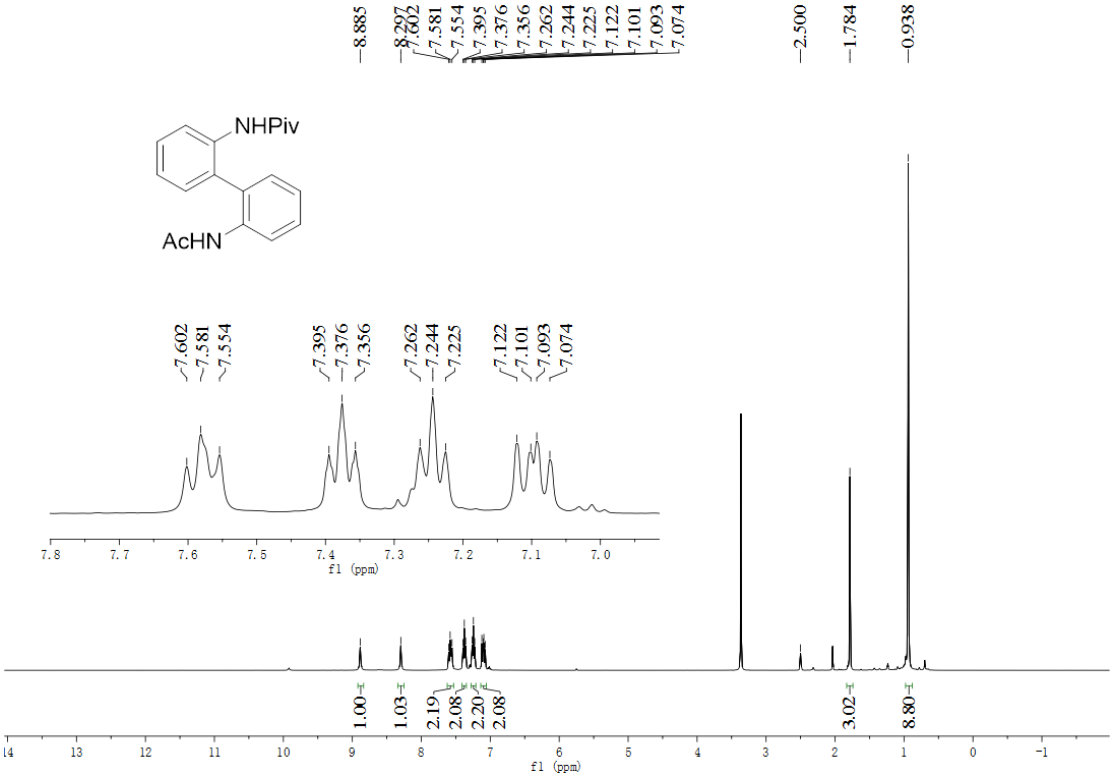
VI. References

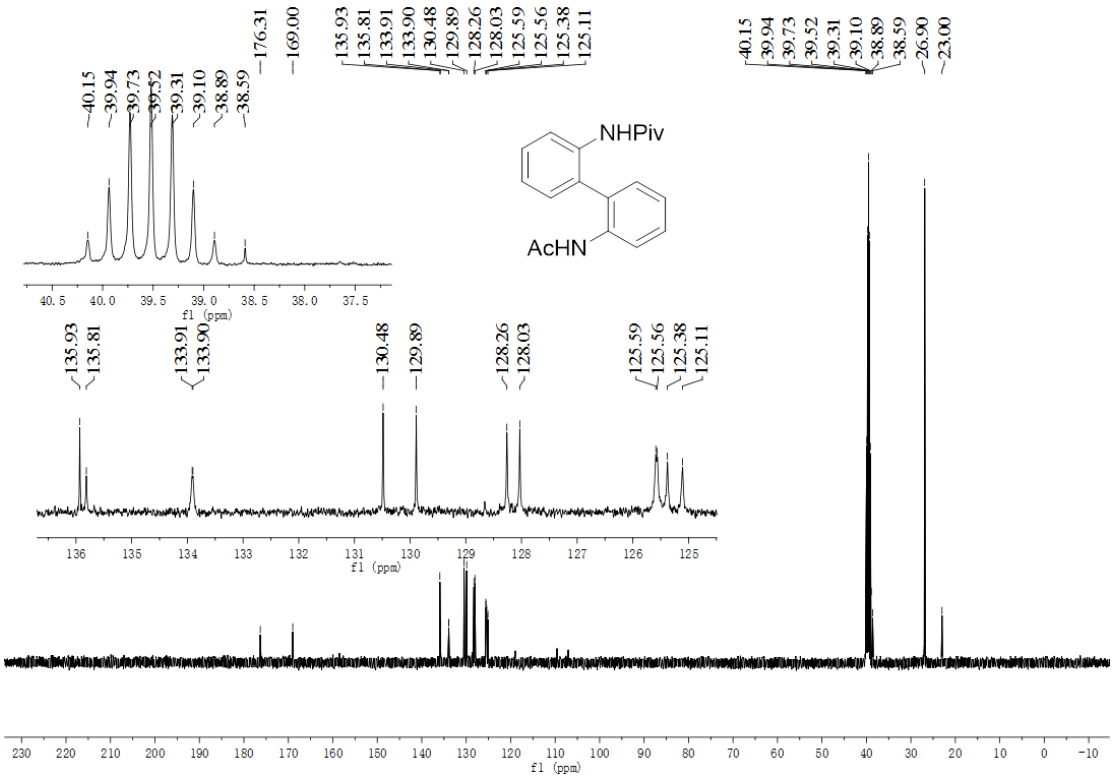
(1) J. Park and S. Chang, *Angew. Chem. Int. Ed*. 2015, **54**, 14103.

(2) M.-L. Louillat, A. Biafora, F. Legros and F. W. Patureau, *Angew. Chem. Int. Ed*. 2014, **53**, 3505.

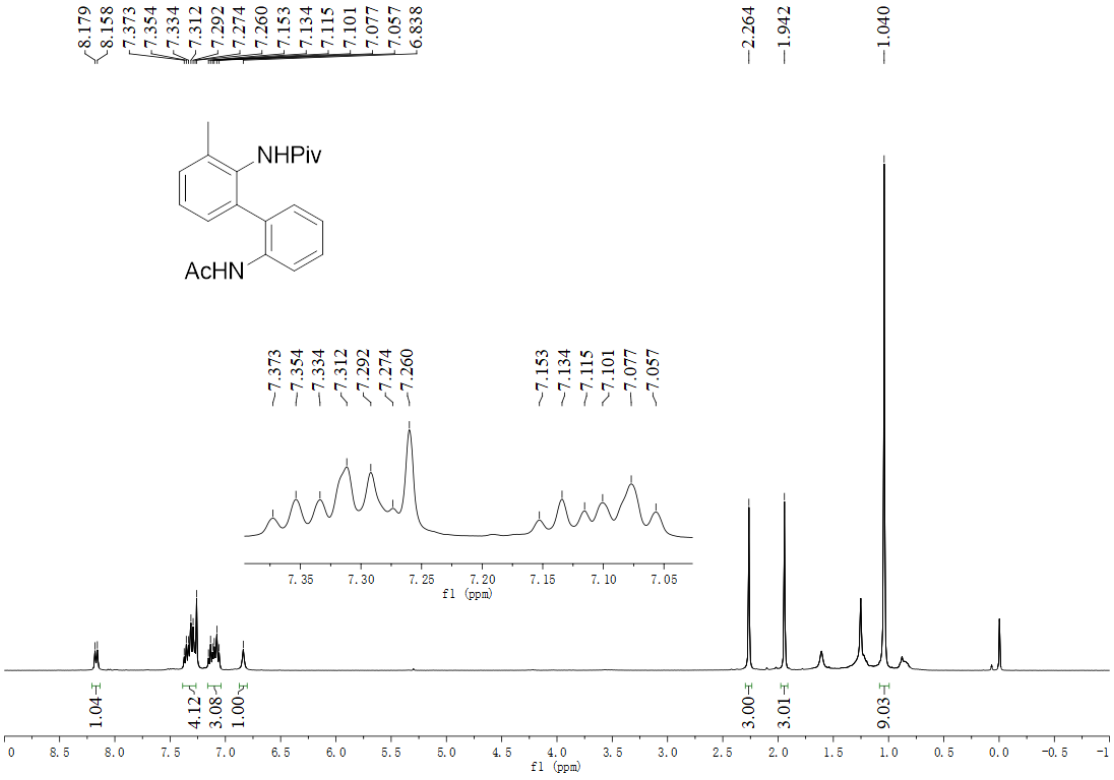
VII. Copies of ^{1}H and ^{13}C NMR spectra

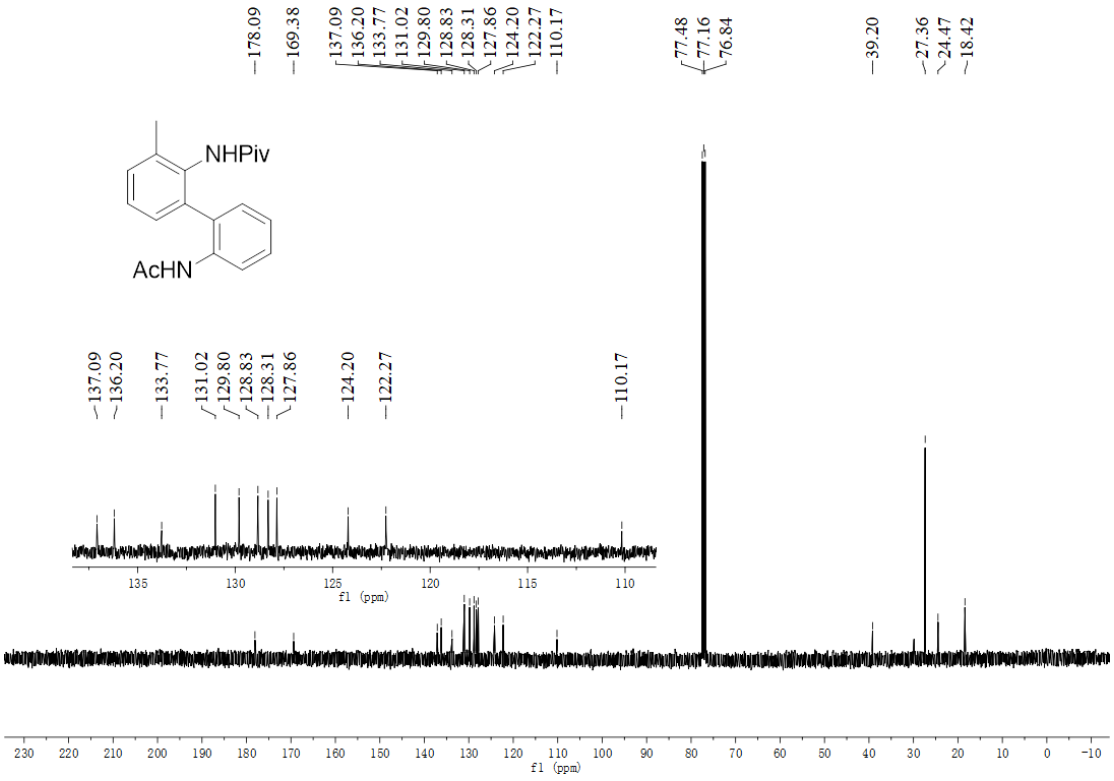
N-(2'-Acetamido-[1,1'-biphenyl]-2-yl)pivalamide (3a)



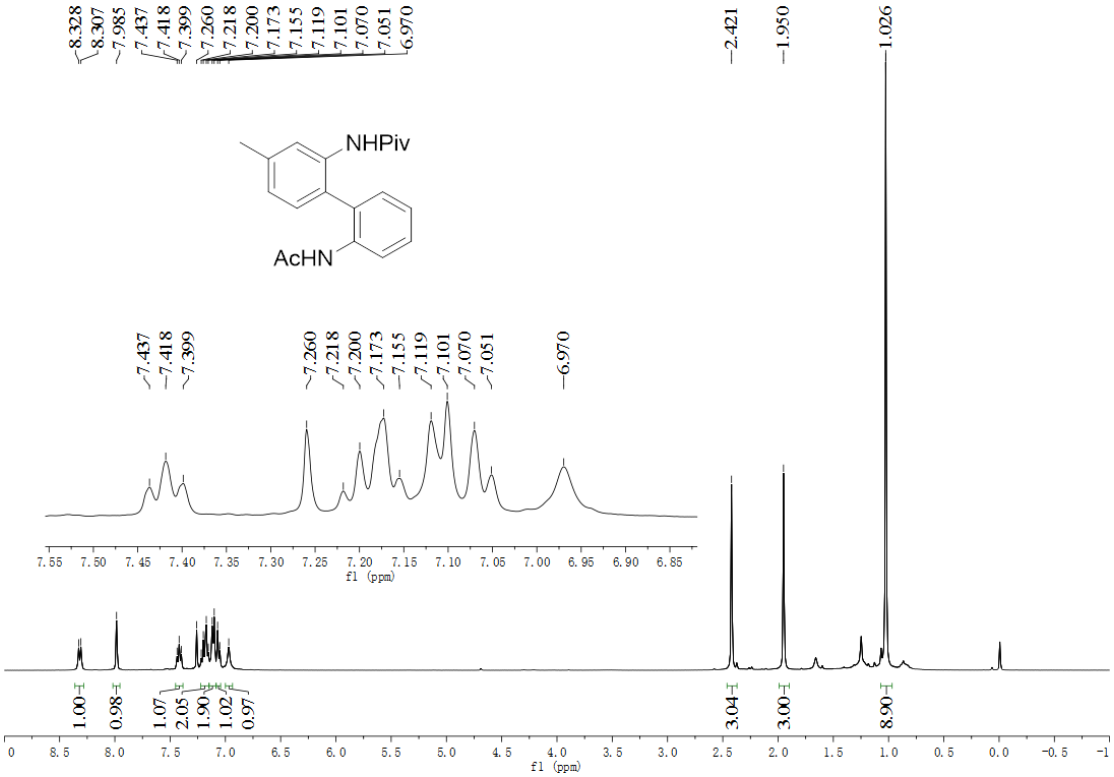


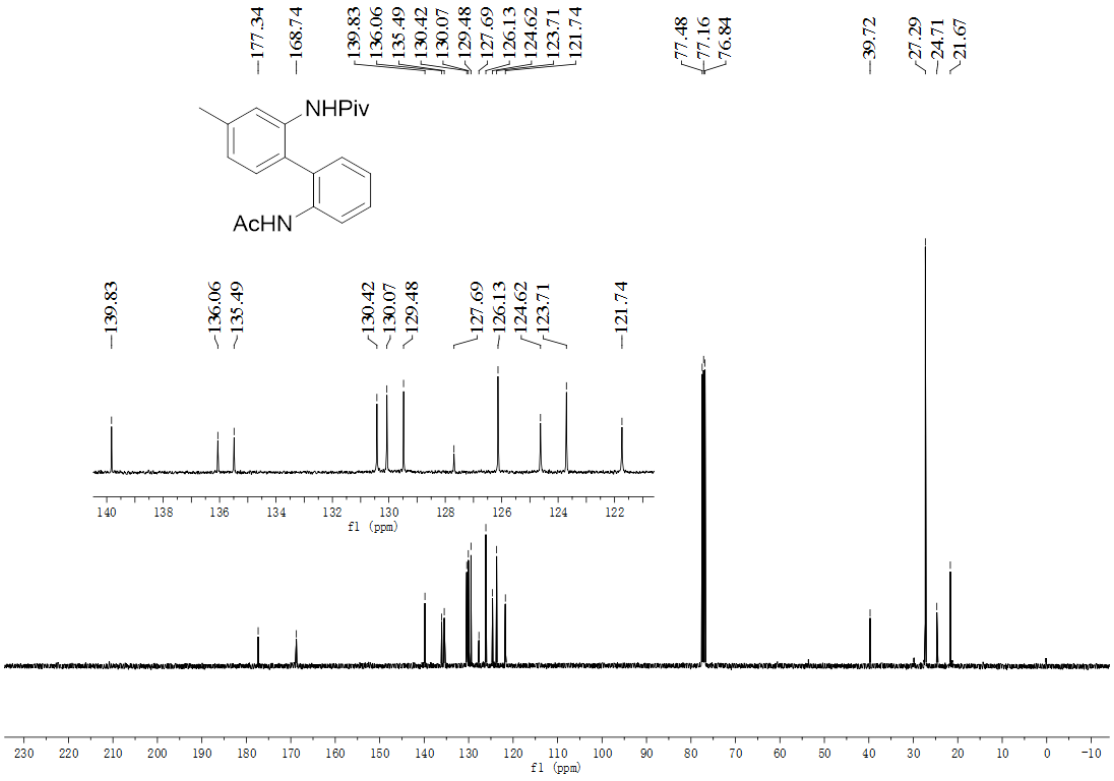
N-(2'-Acetamido-3-methyl-[1,1'-biphenyl]-2-yl)pivalamide (3b)



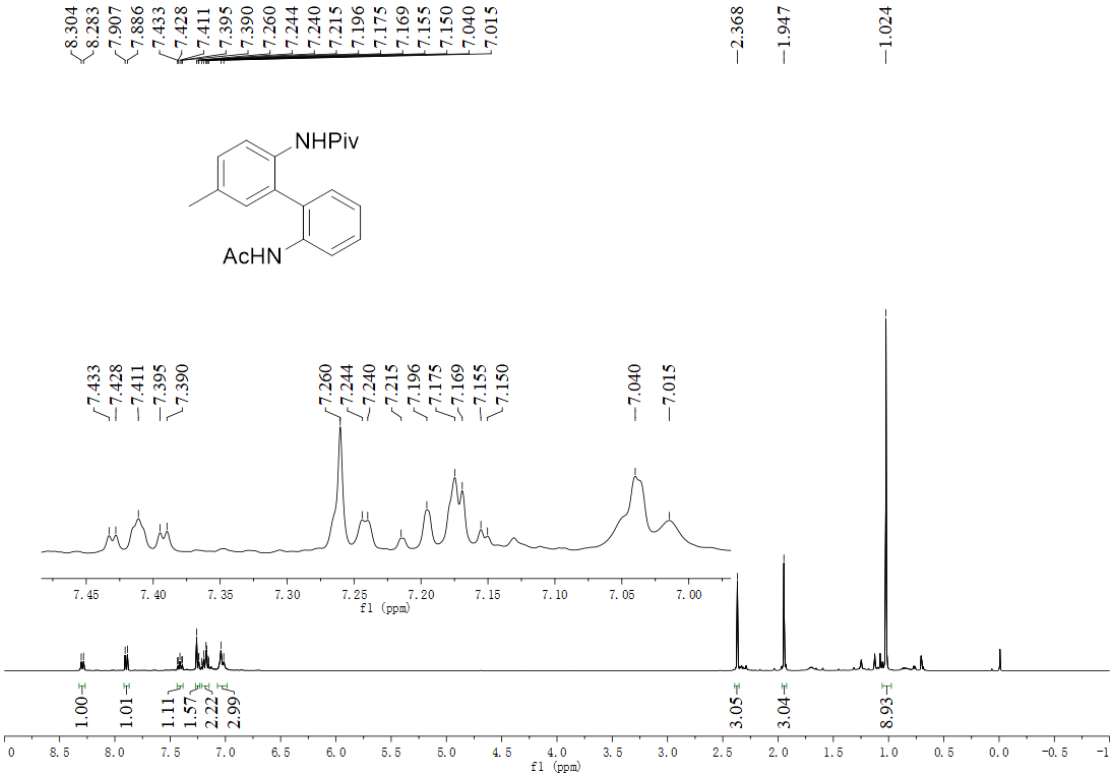


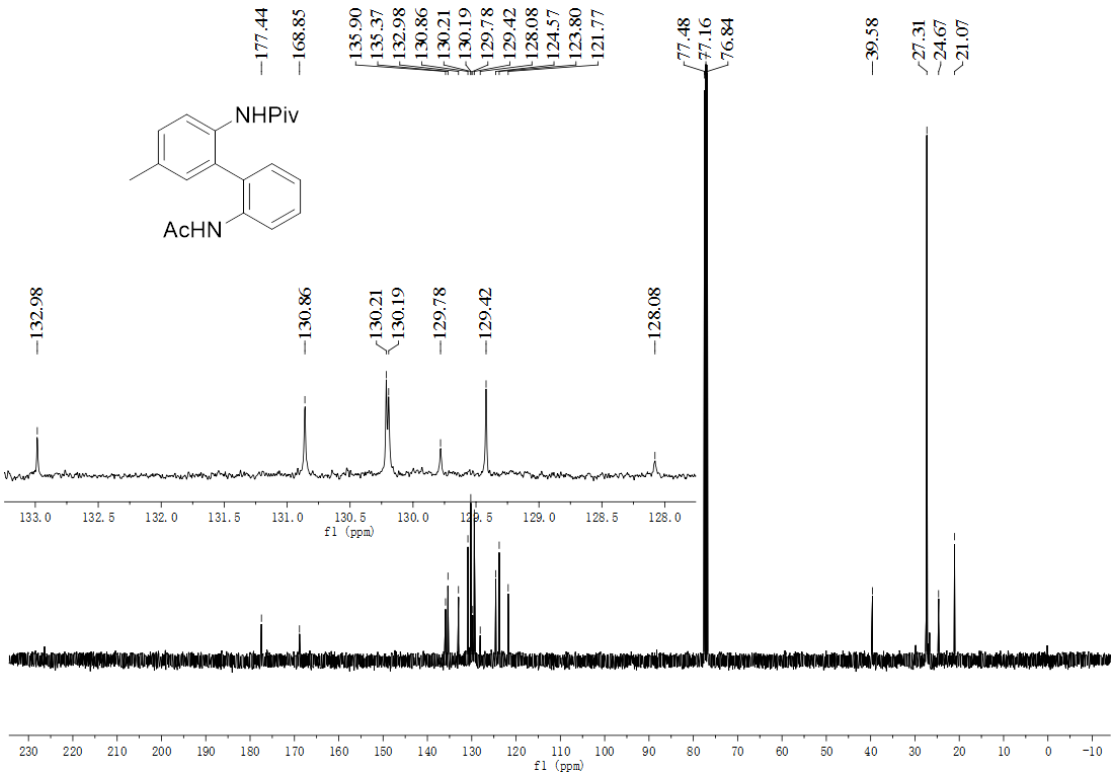
N-(2'-Acetamido-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide (3c)



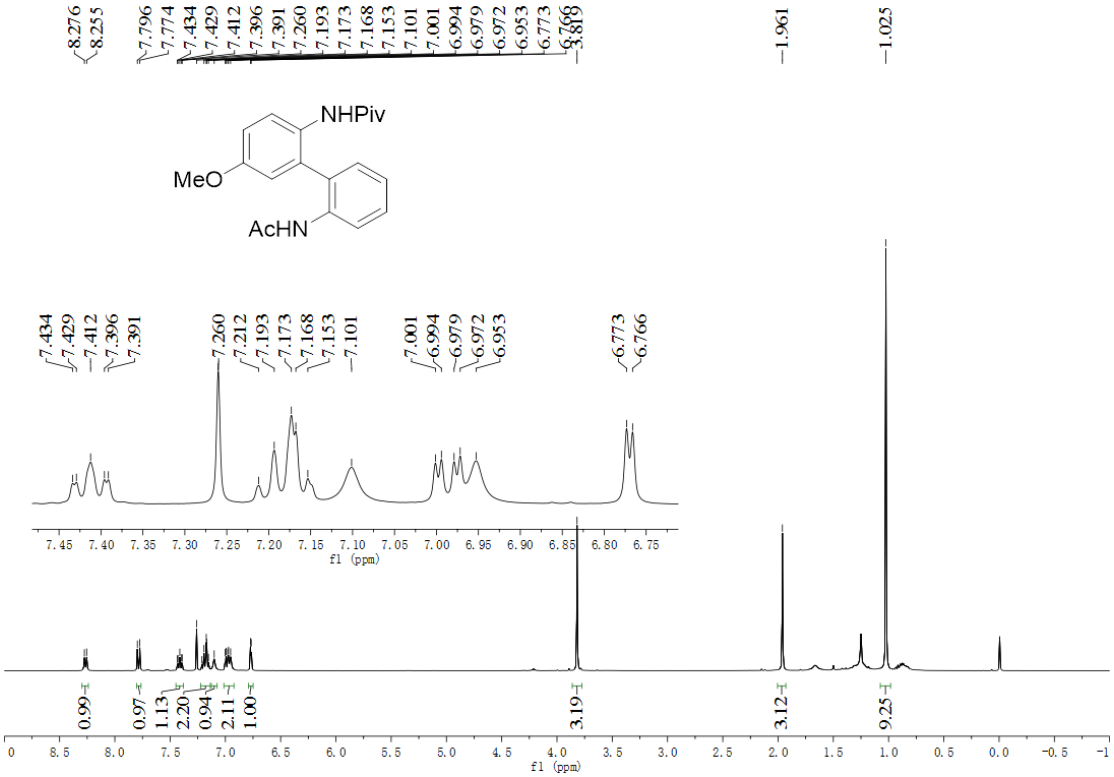


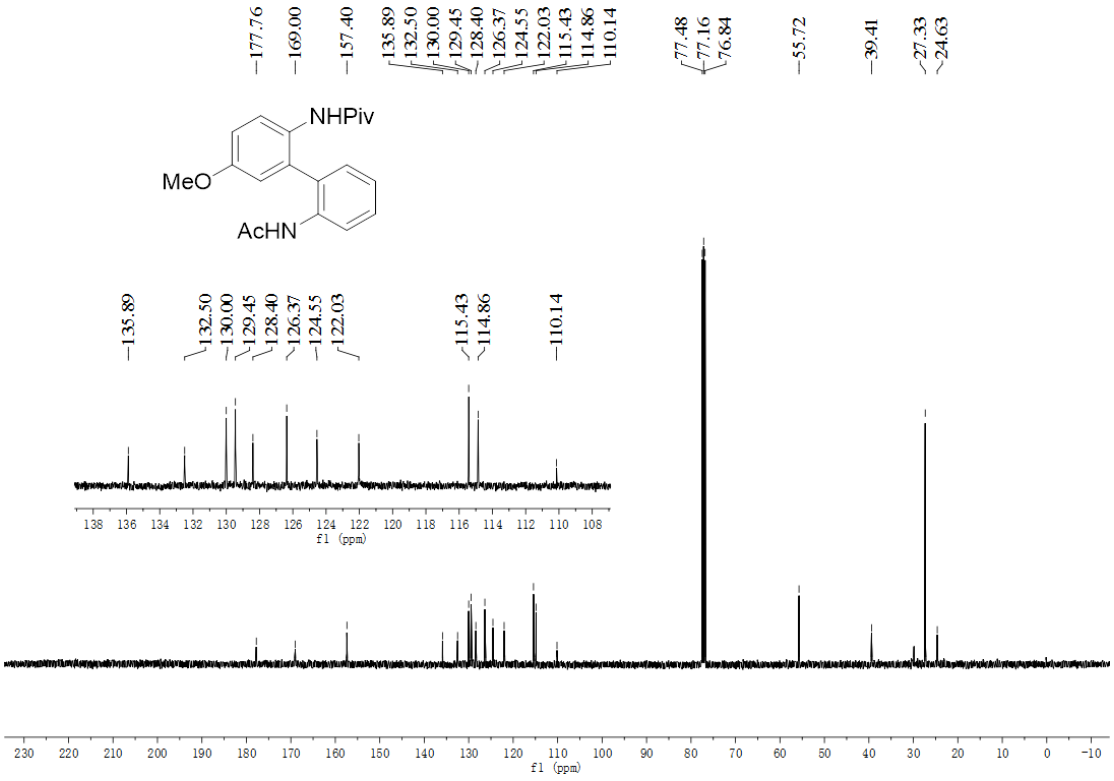
N-(2'-Acetamido-5-methyl-[1,1'-biphenyl]-2-yl)pivalamide (3d)



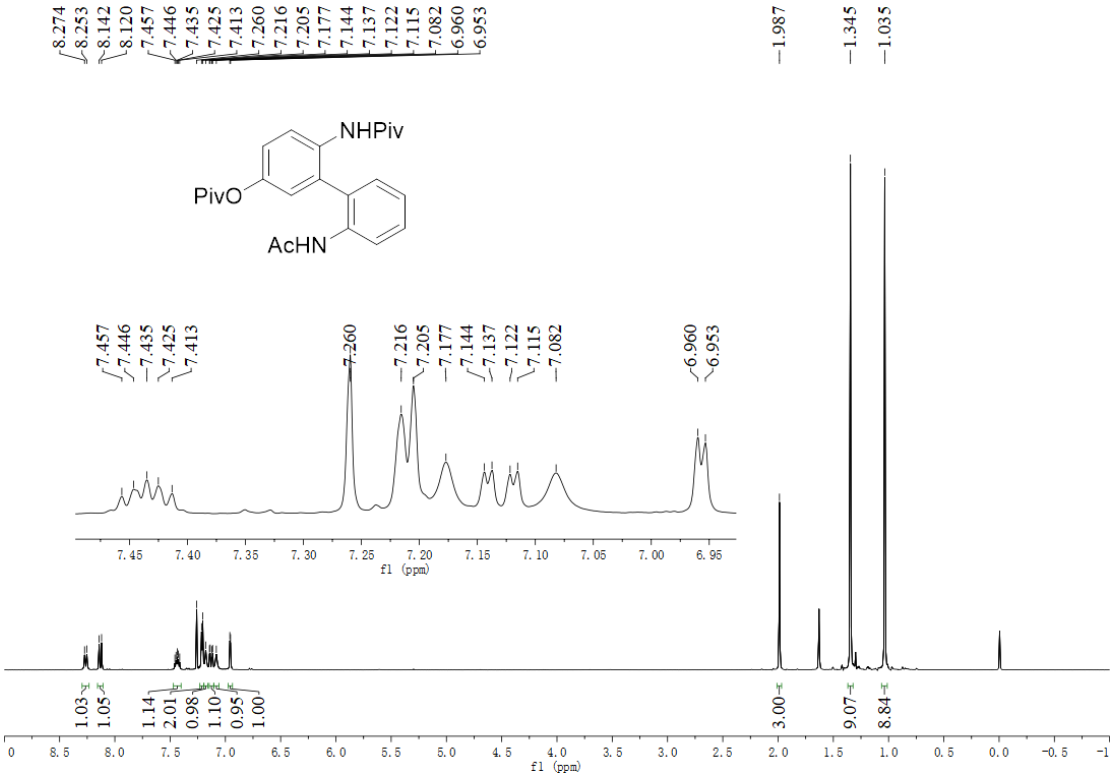


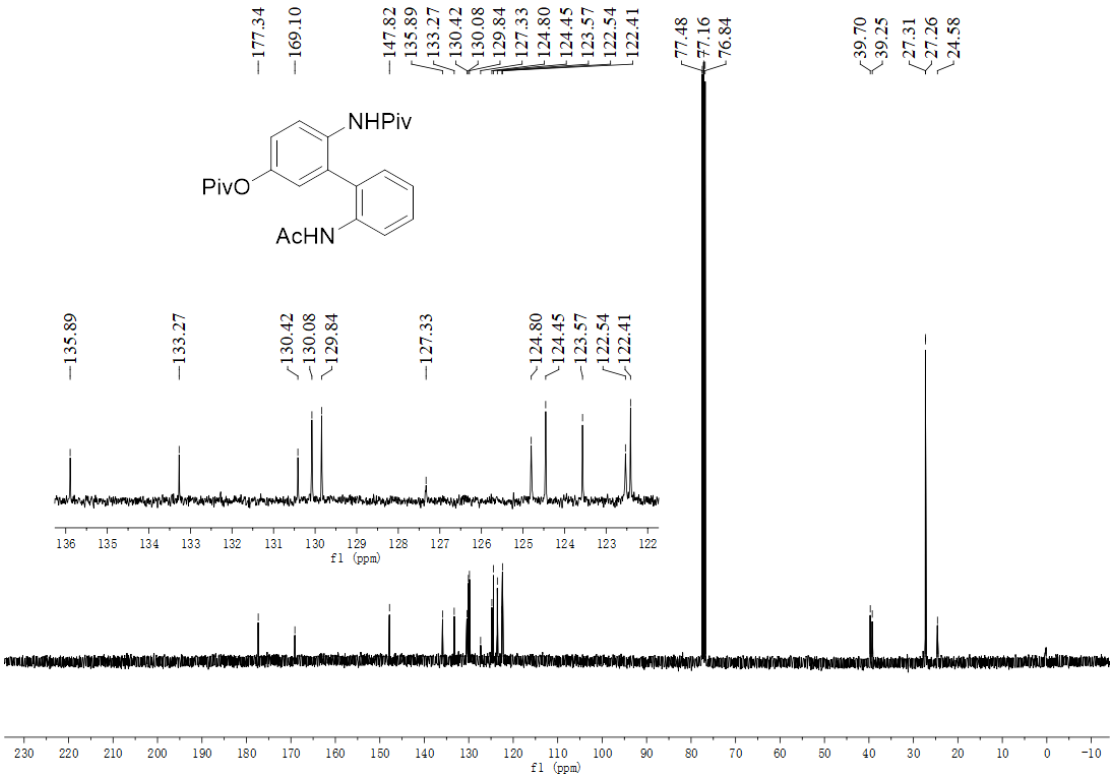
N-(2'-Acetamido-5-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (3e)



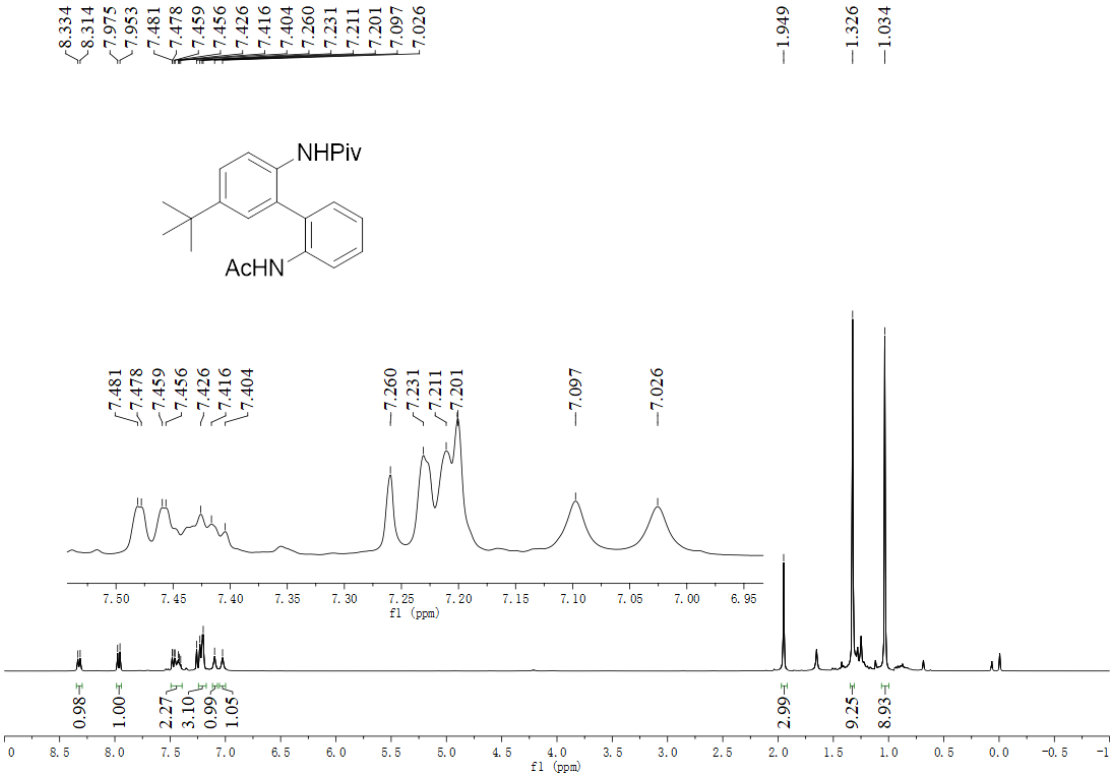


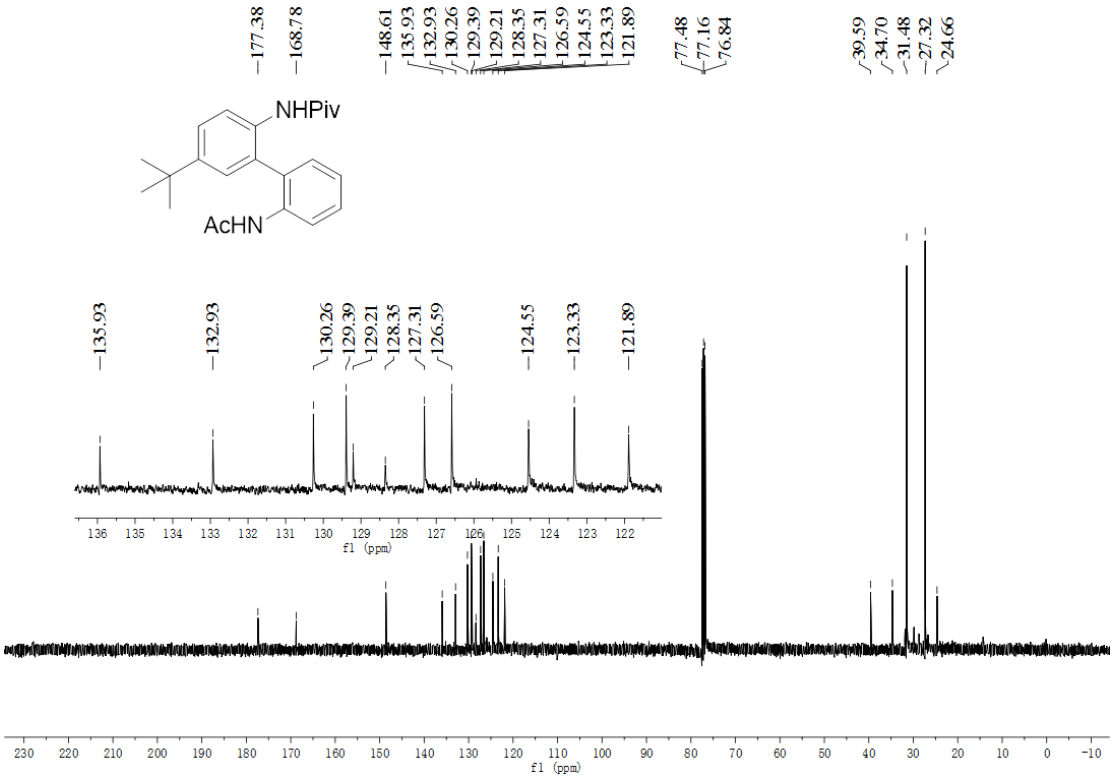
2'-Acetamido-6-pivalamido-[1,1'-biphenyl]-3-yl pivalate (3f)



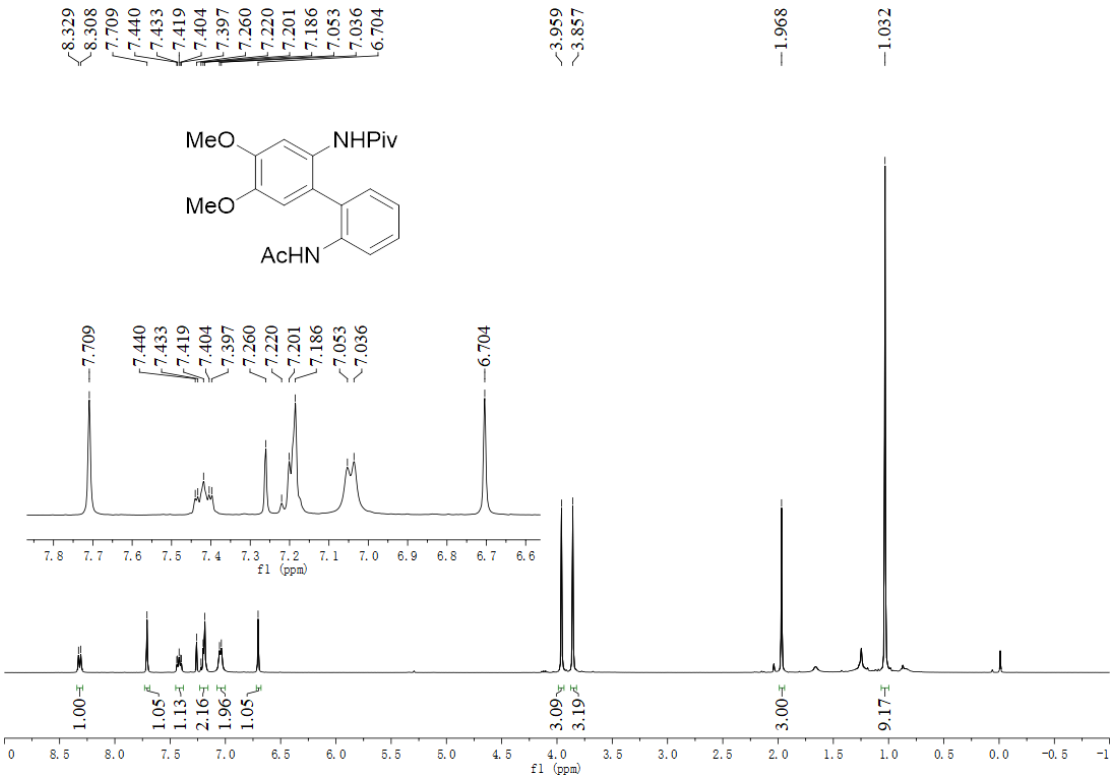


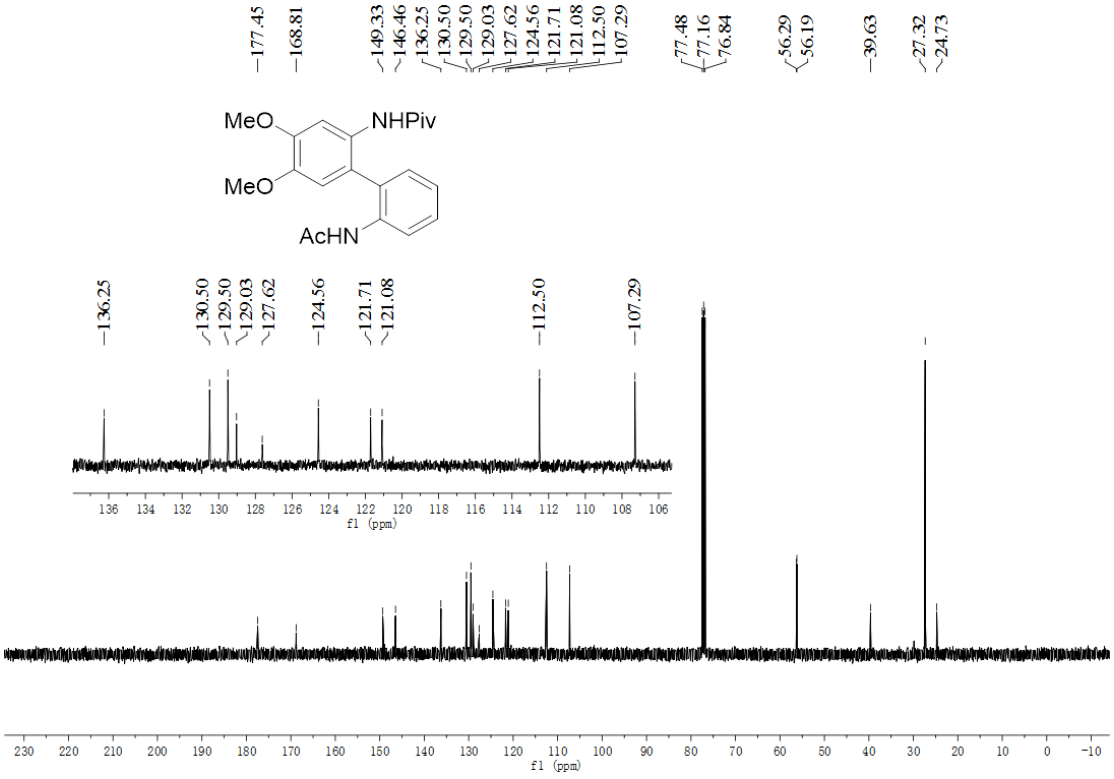
N-(2'-Acetamido-5-(*tert*-butyl)-[1,1'-biphenyl]-2-yl)pivalamide (3g)



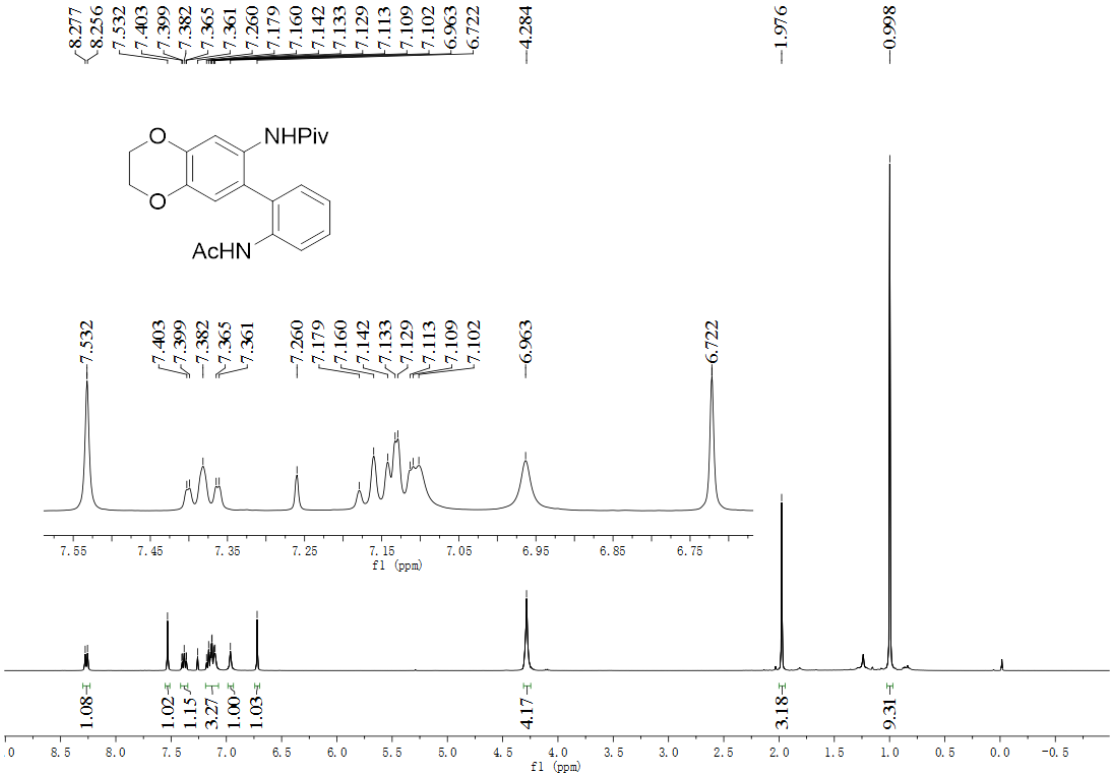


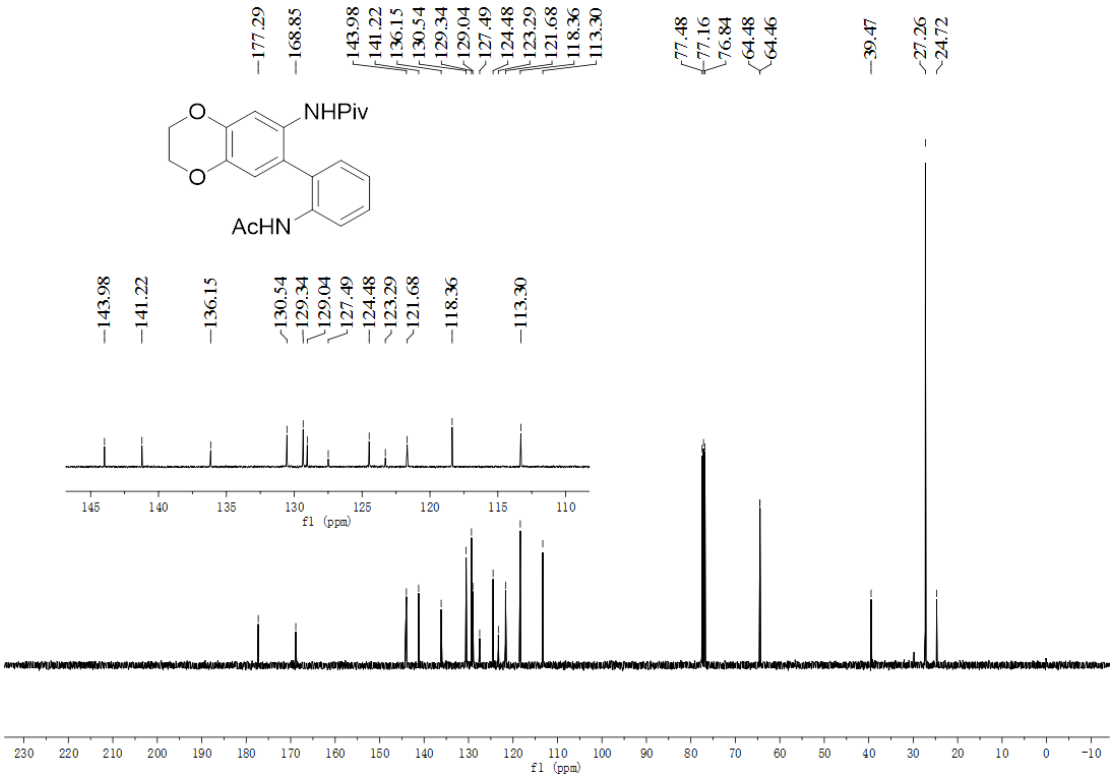
N-(2'-Acetamido-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)pivalamide (3h)



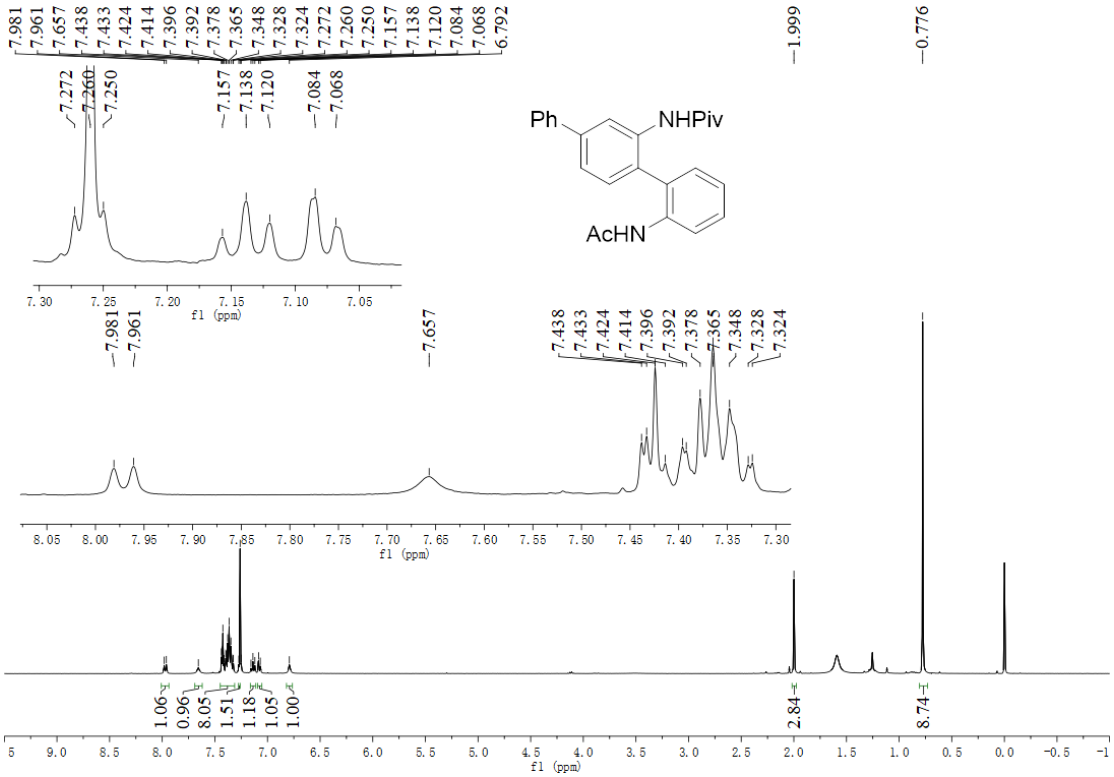


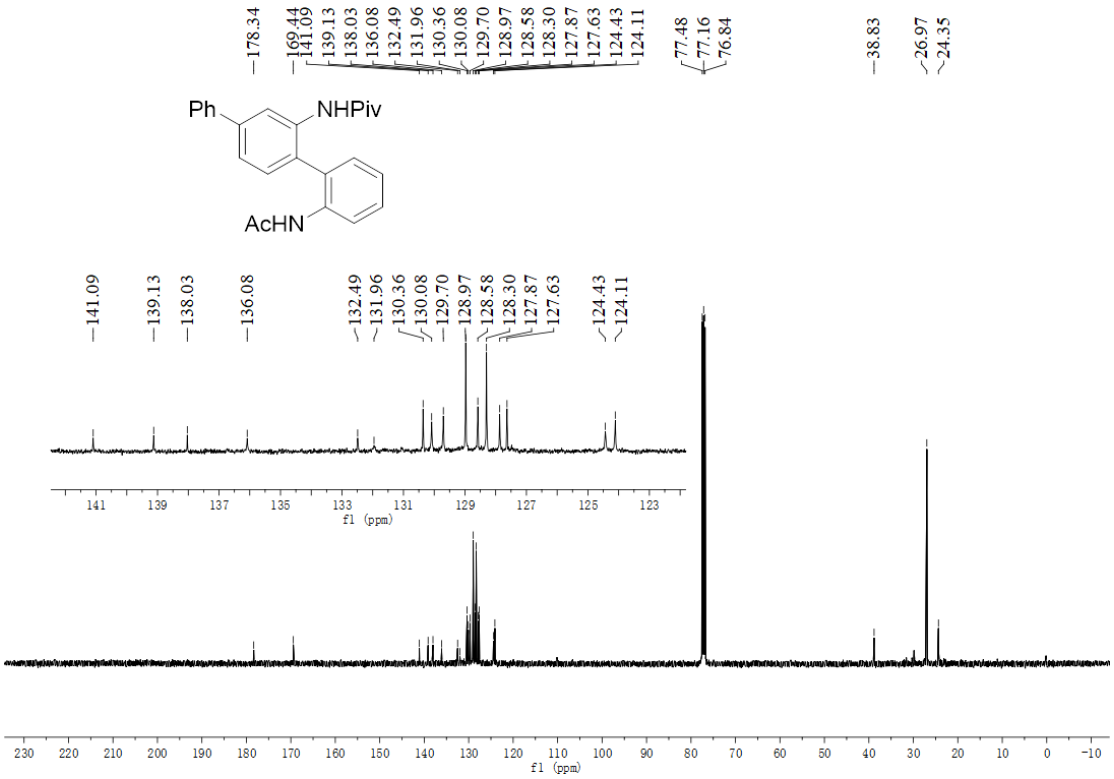
N-(7-(2-Acetamidophenyl)-2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)pivalamide (3i)



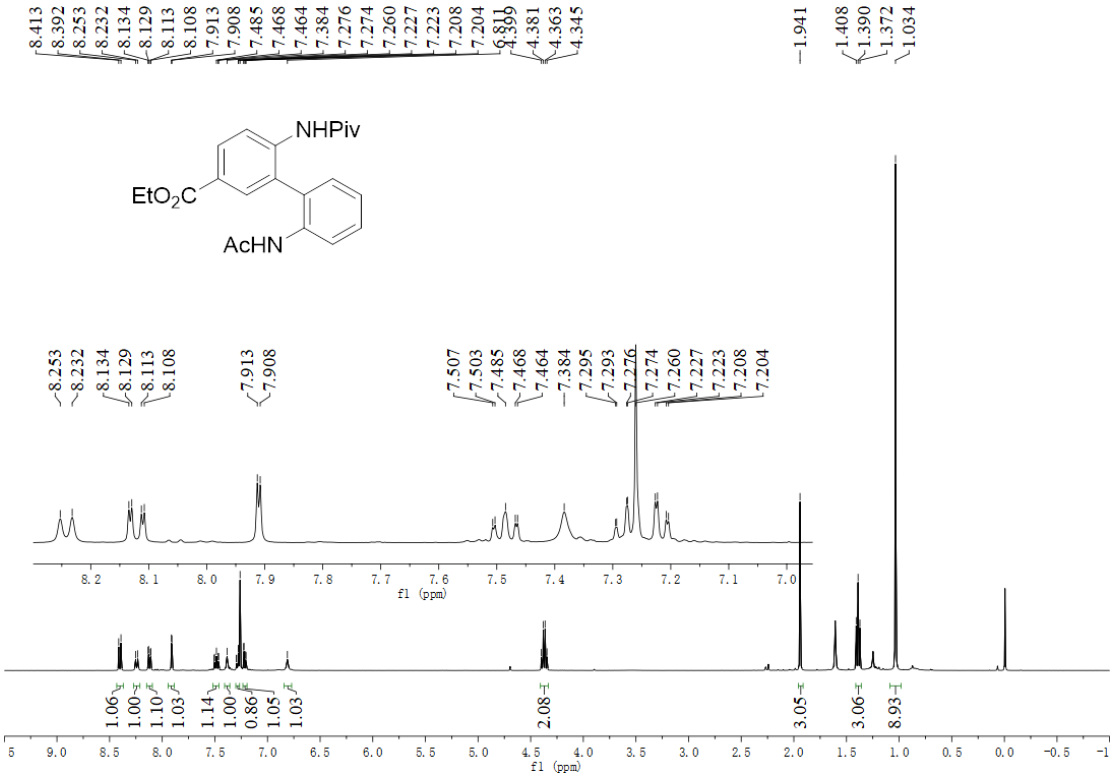


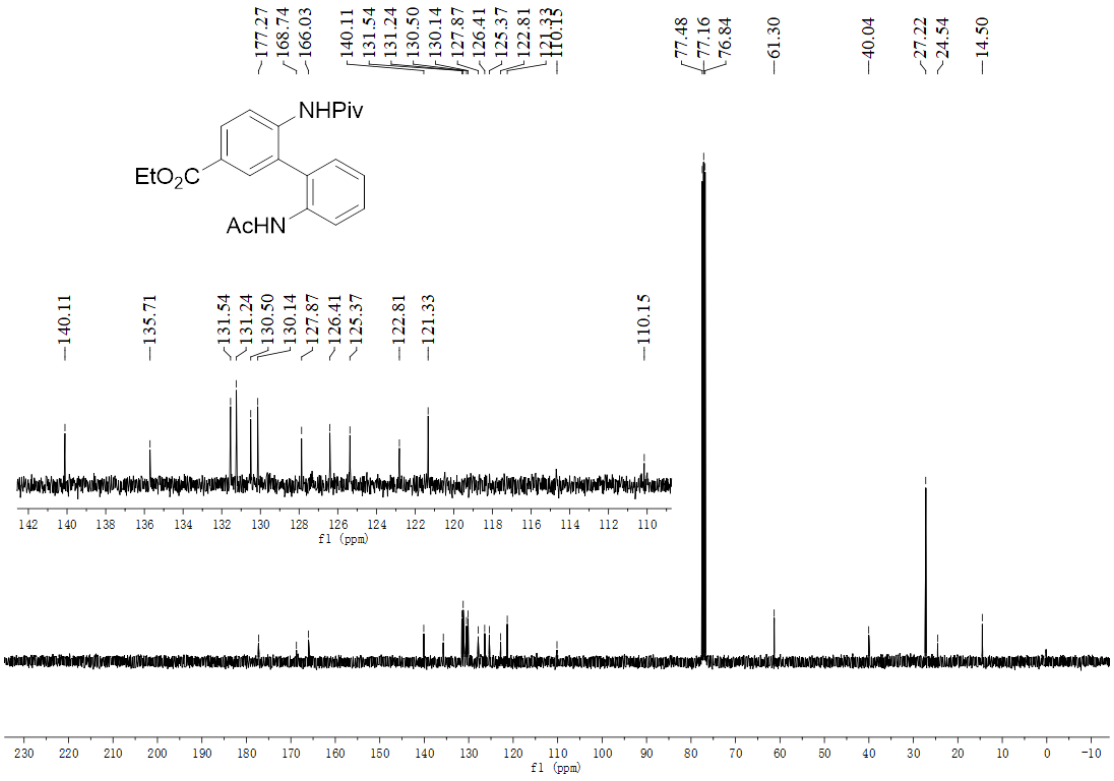
N-(2-Acetamido-[1,1':4',1''-terphenyl]-2'-yl)pivalamide (3j)



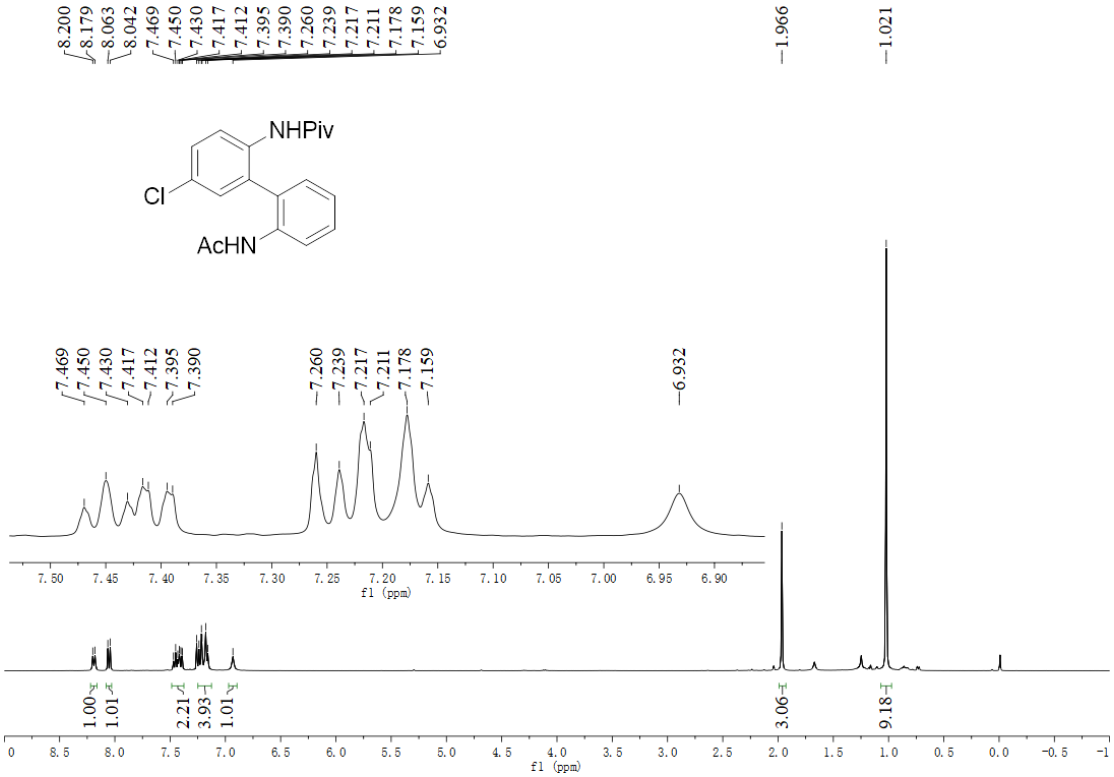


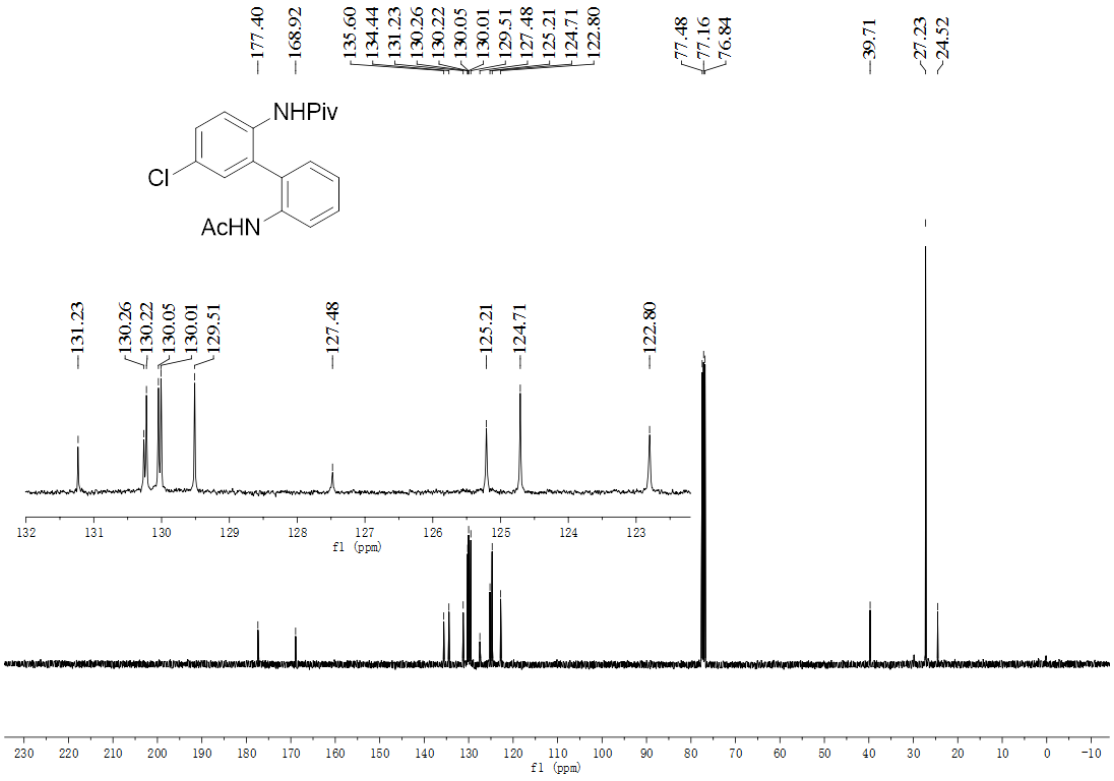
Ethyl 2'-acetamido-6-pivalamido-[1,1'-biphenyl]-3-carboxylate (3k)



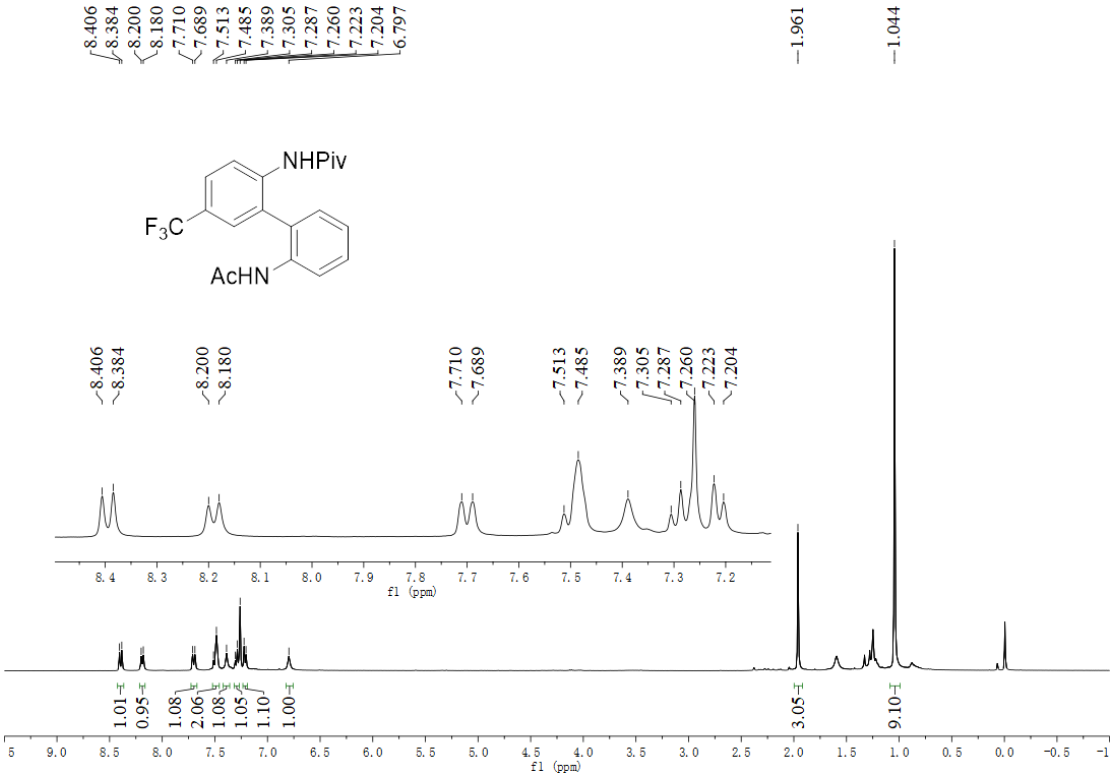


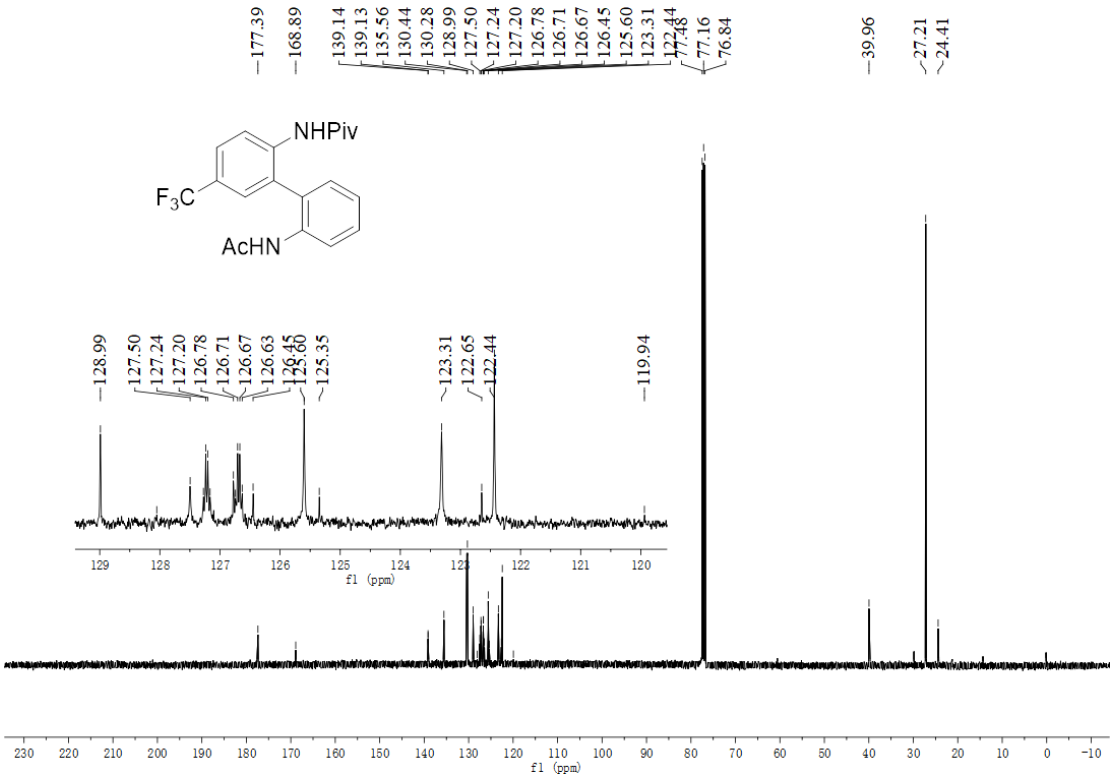
N-(2'-Acetamido-5-chloro-[1,1'-biphenyl]-2-yl)pivalamide (3l)



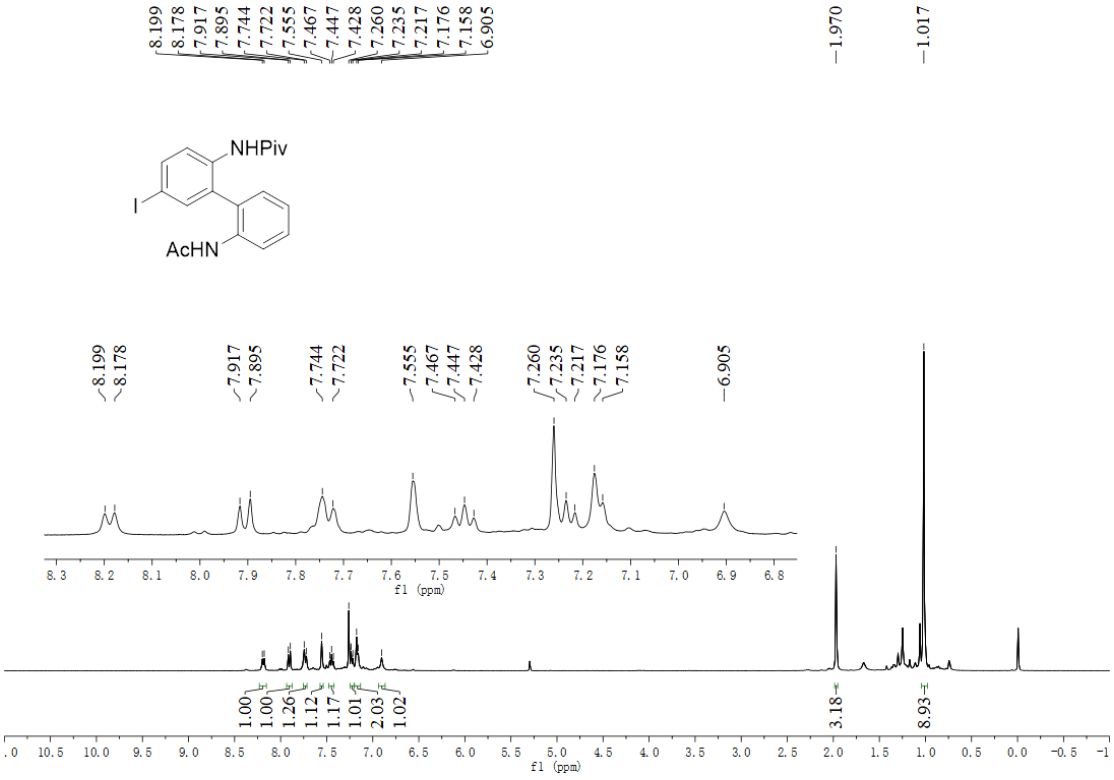


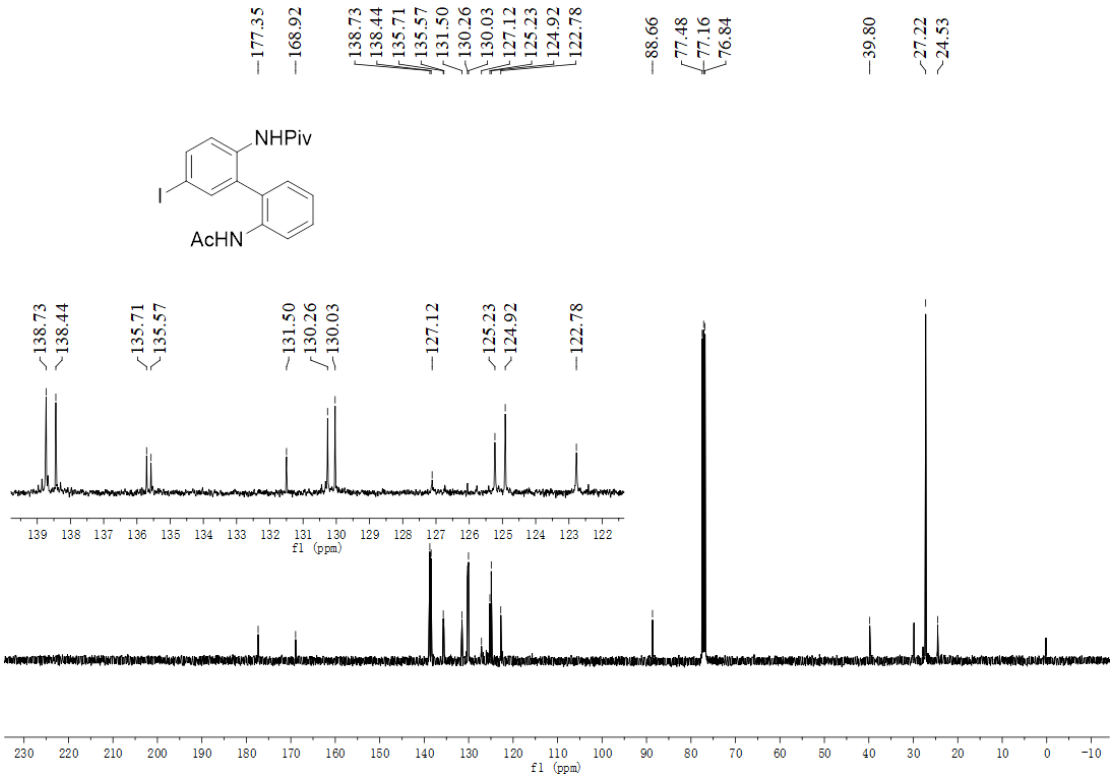
N-(2'-Acetamido-5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamide (3m)



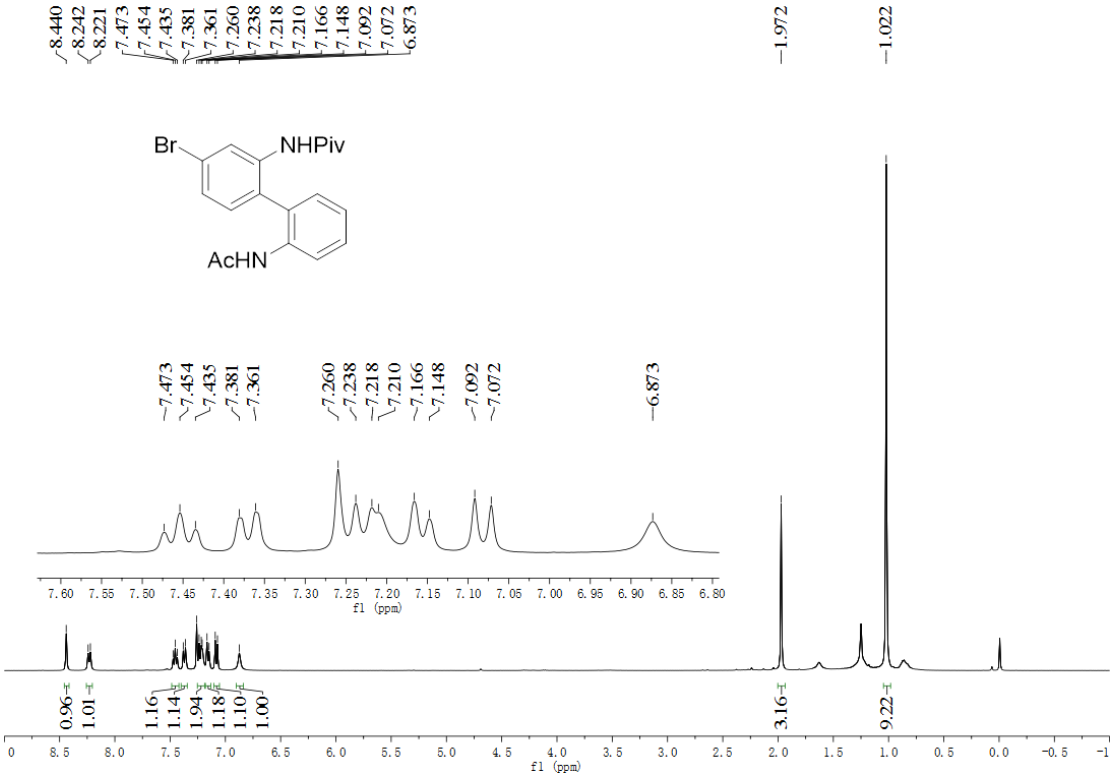


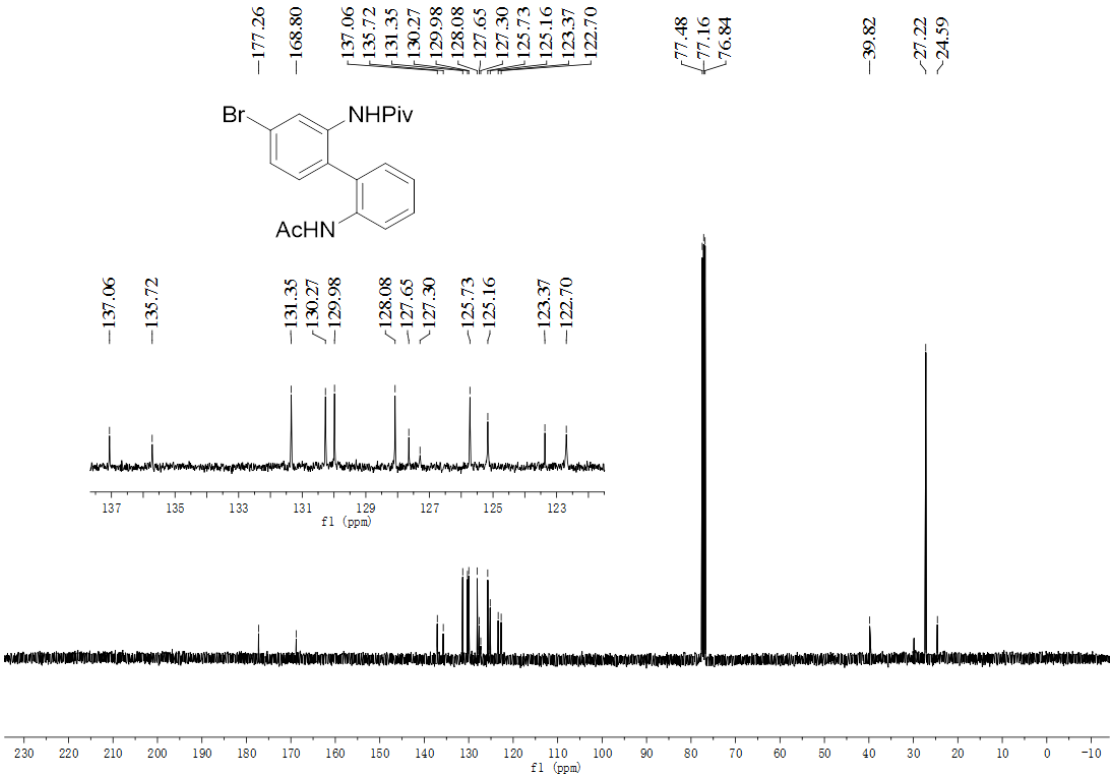
N-(2'-Acetamido-5-iodo-[1,1'-biphenyl]-2-yl)pivalamide (3n)



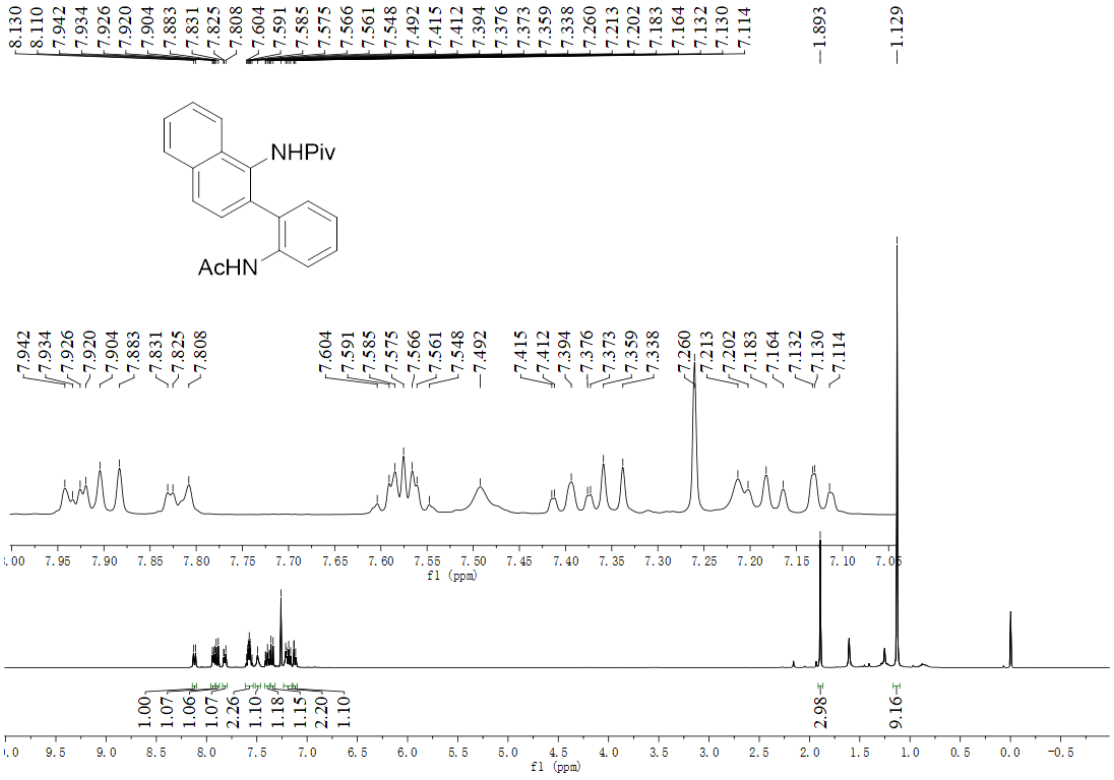


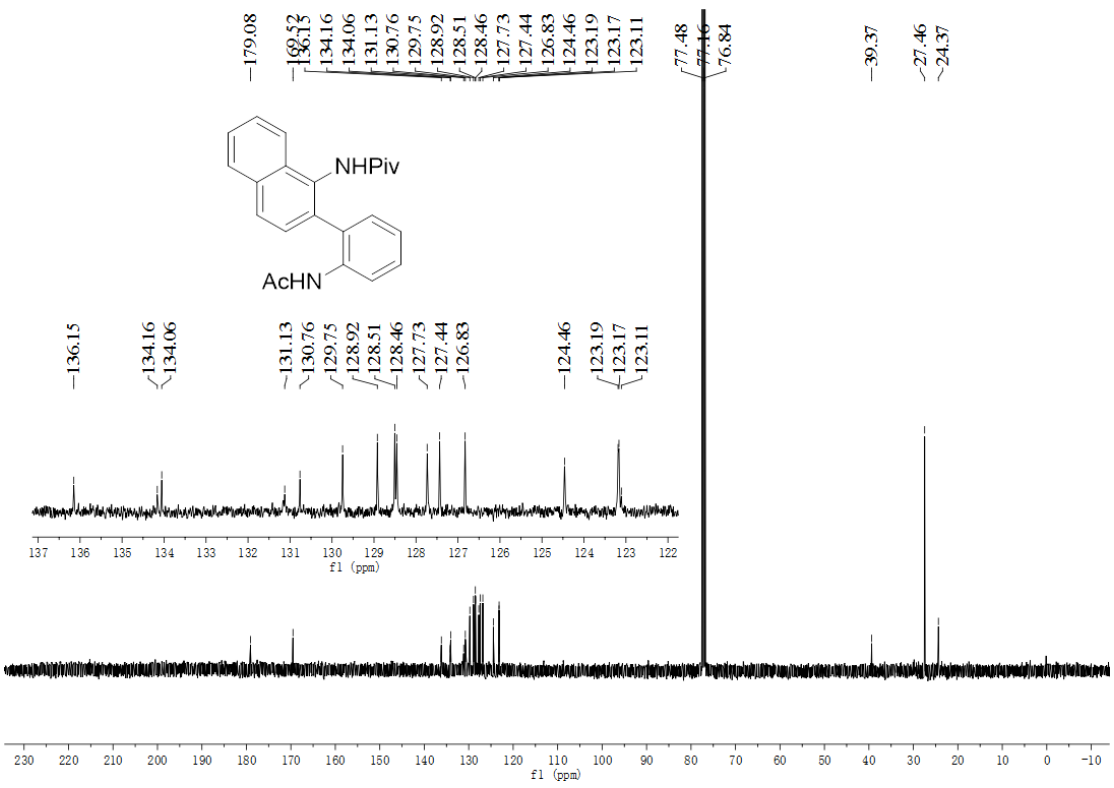
N-(2'-Acetamido-4-bromo-[1,1'-biphenyl]-2-yl)pivalamide (3o)



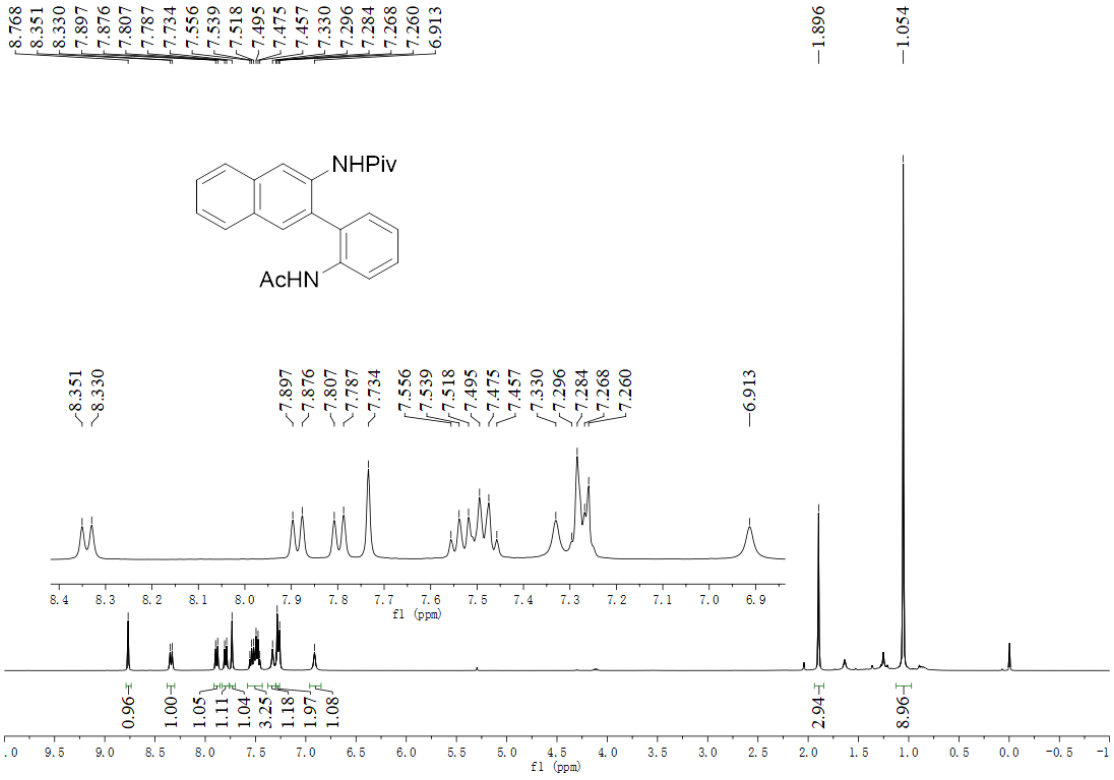


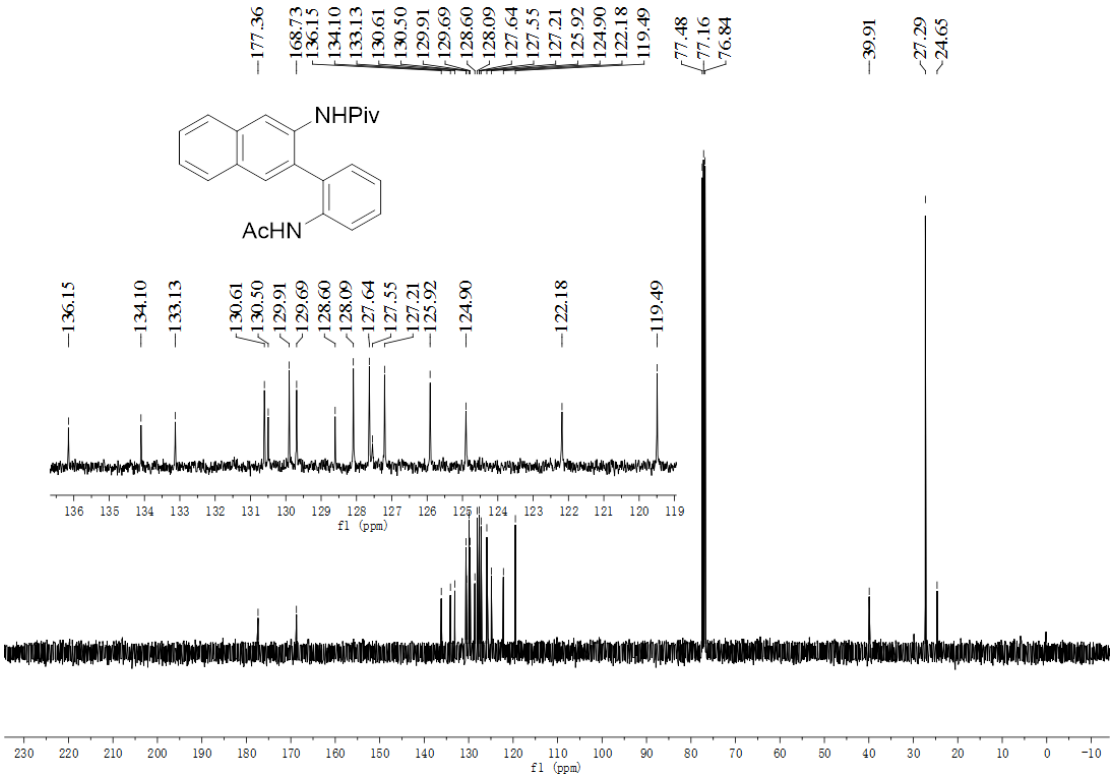
N-(2-(2-Acetamidophenyl)naphthalen-1-yl)pivalamide (3p)



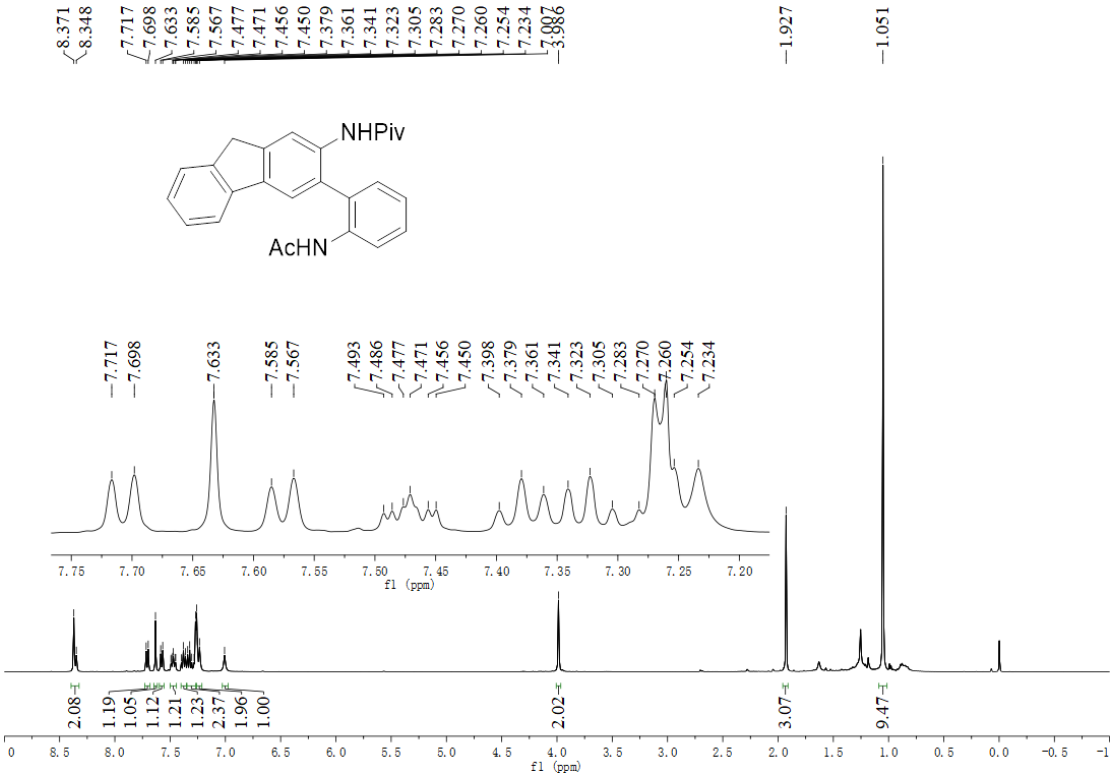


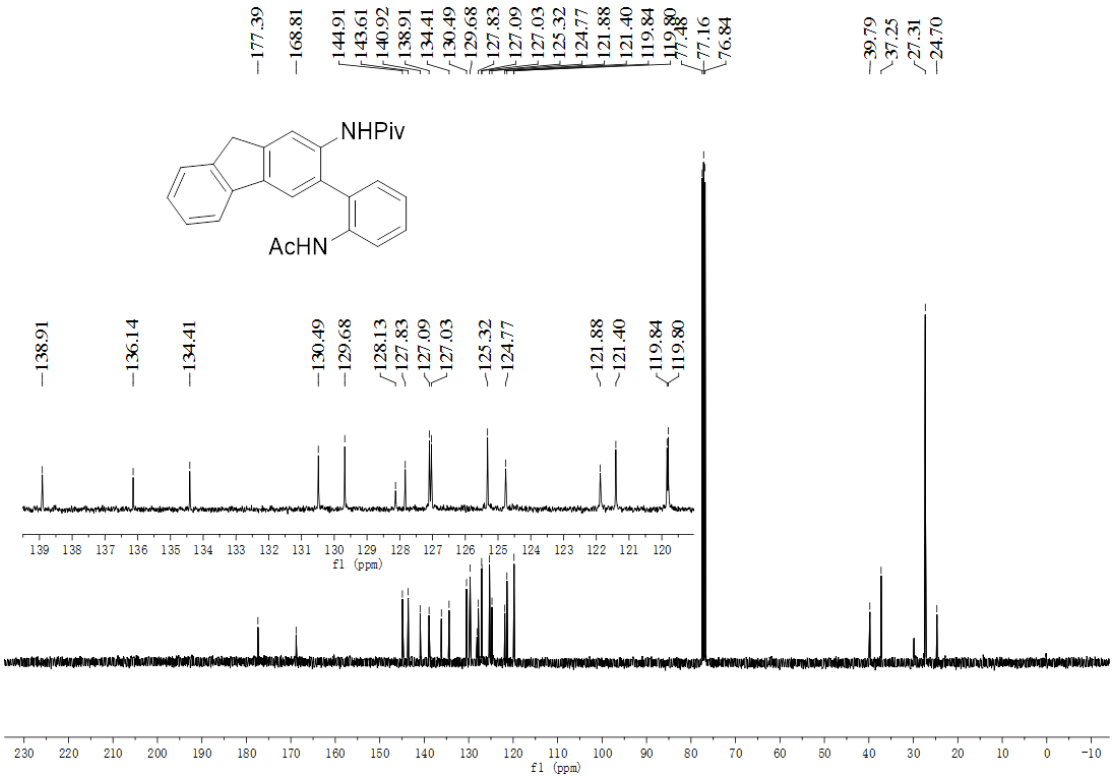
N-(3-(2-Acetamidophenyl)naphthalen-2-yl)pivalamide (3q)



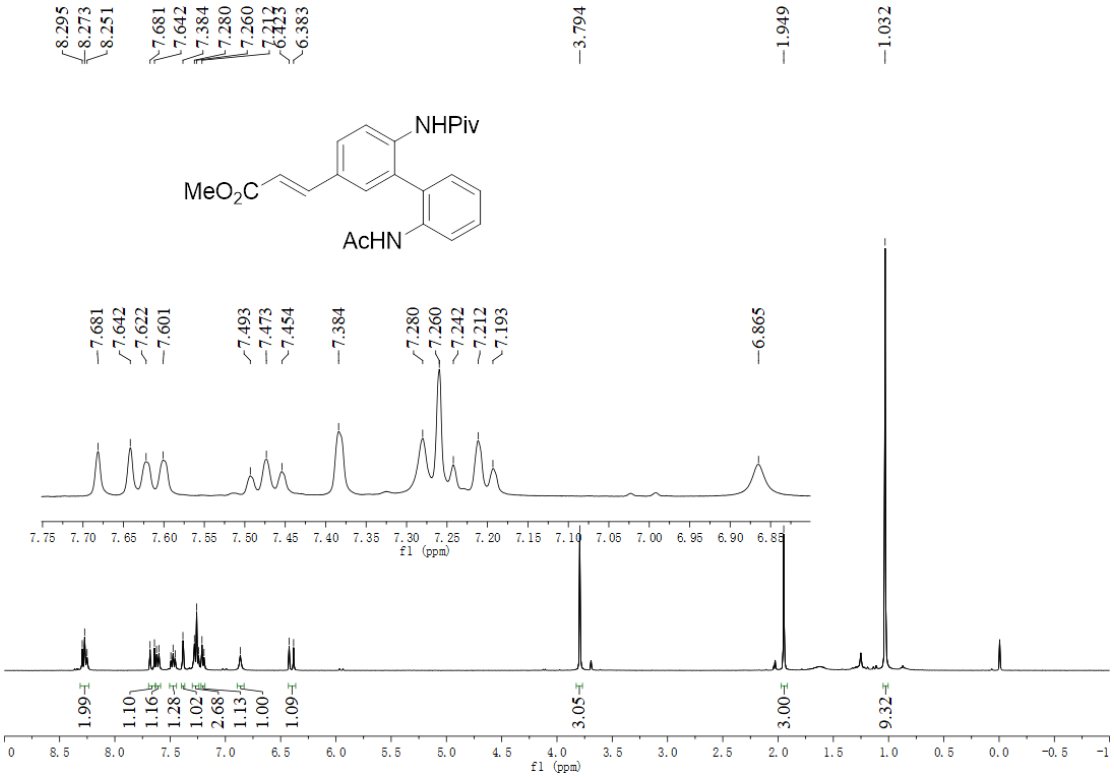


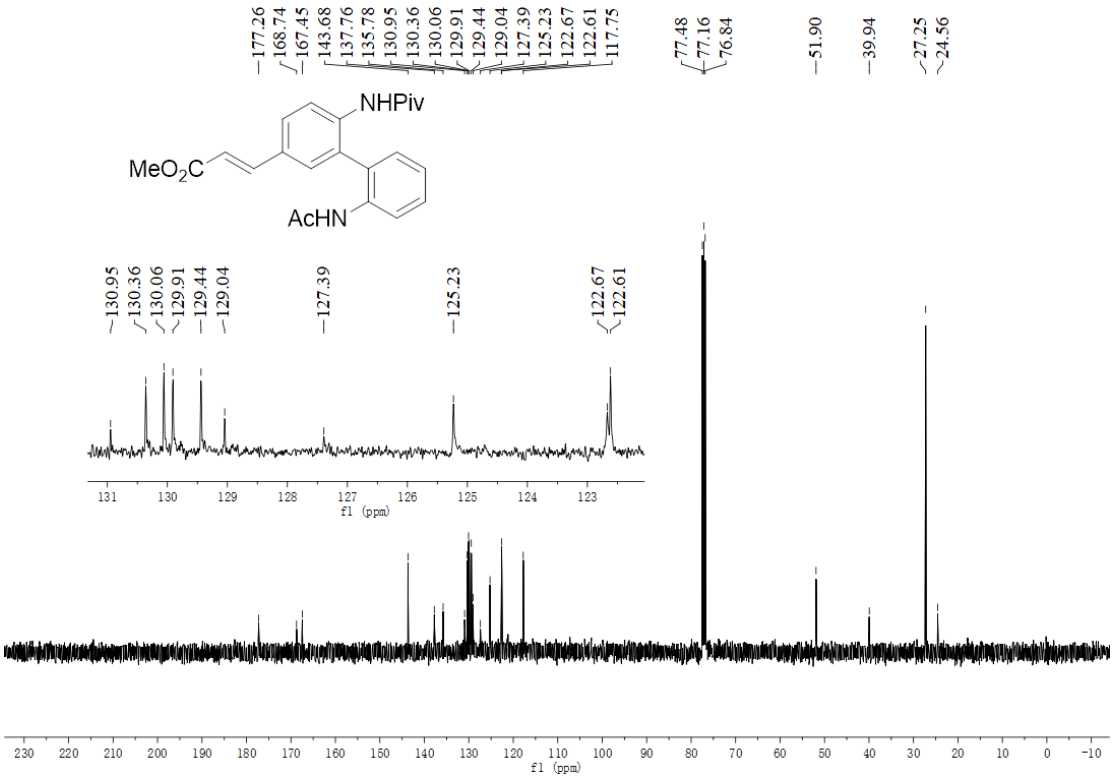
N-(3-(2-Acetamidophenyl)-9*H*-fluoren-2-yl)pivalamide (3r)



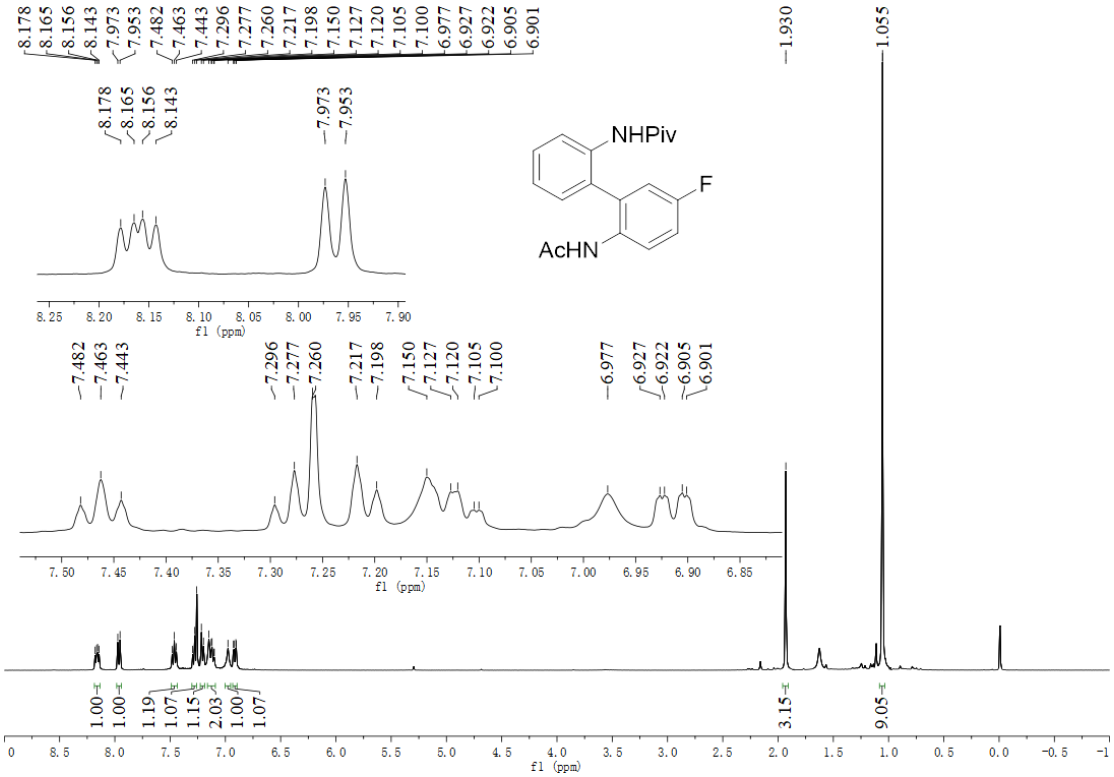


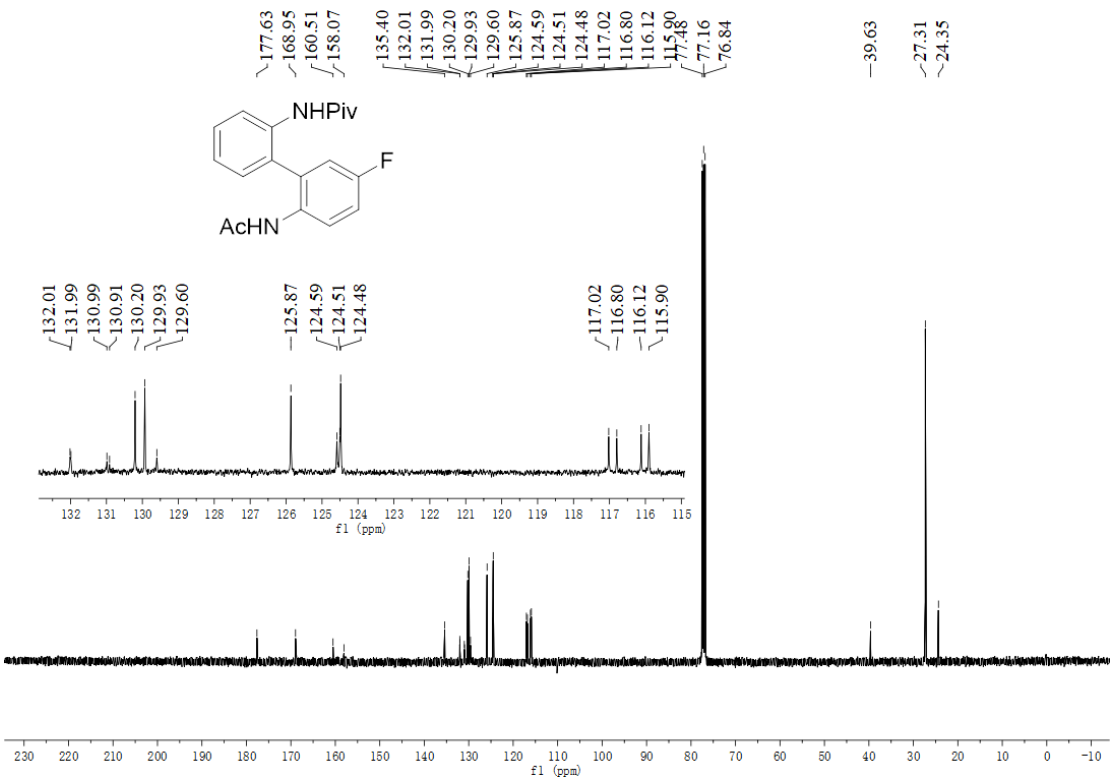
Methyl (*E*)-3-(2'-acetamido-6-pivalamido-[1,1'-biphenyl]-3-yl)acrylate (3s)



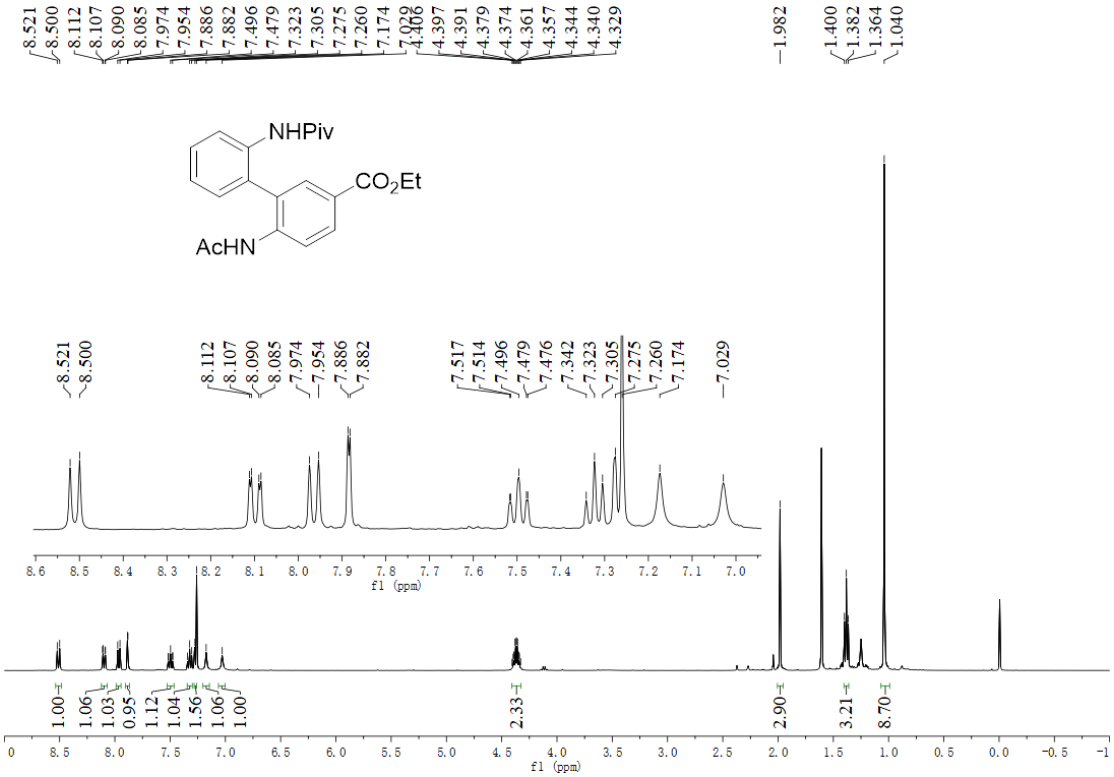


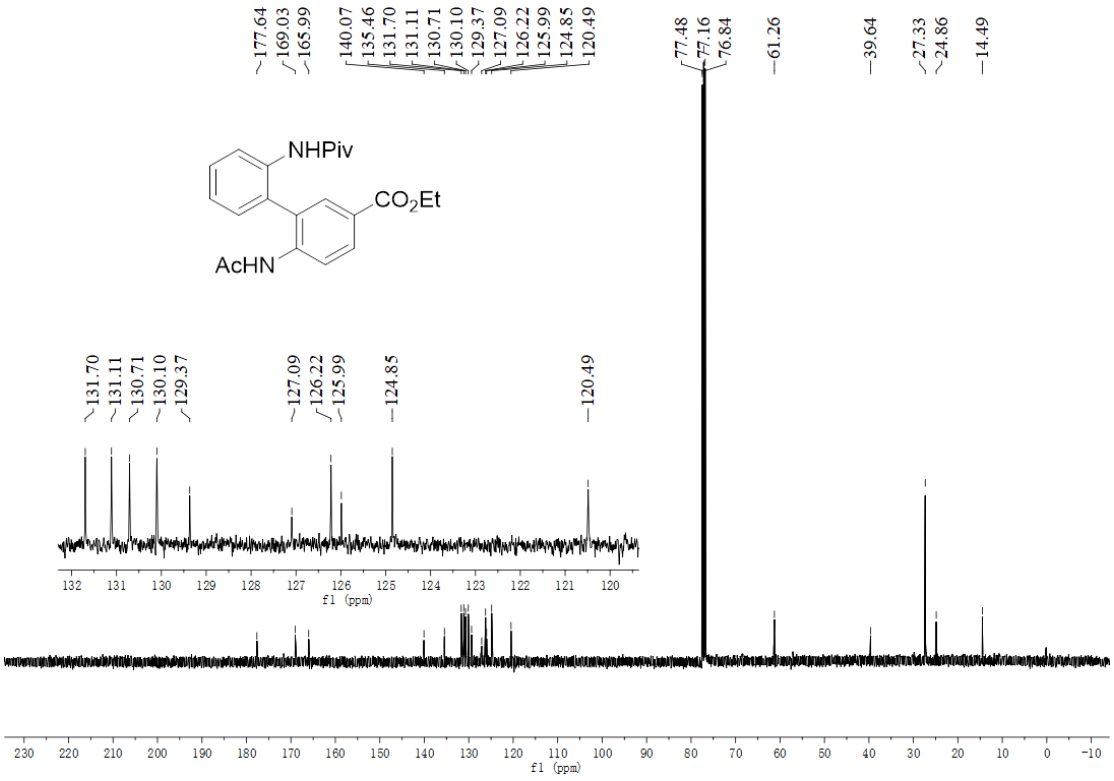
N-(2'-Acetamido-5'-fluoro-[1,1'-biphenyl]-2-yl)pivalamide (4a)



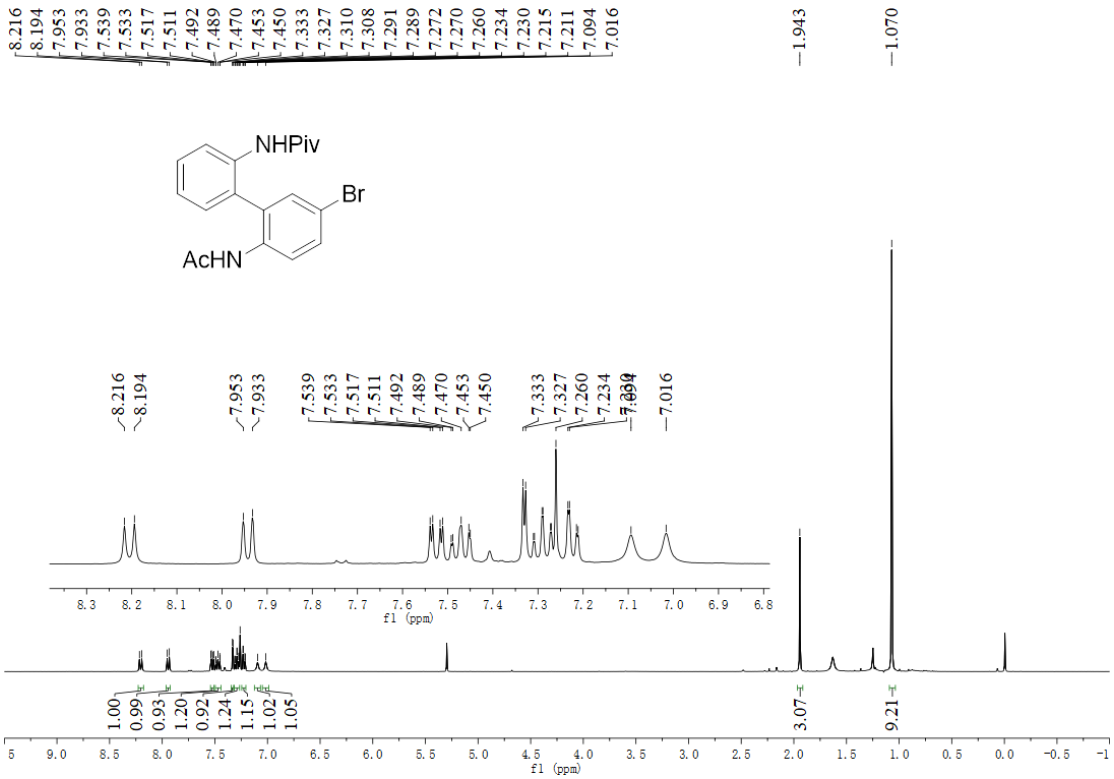


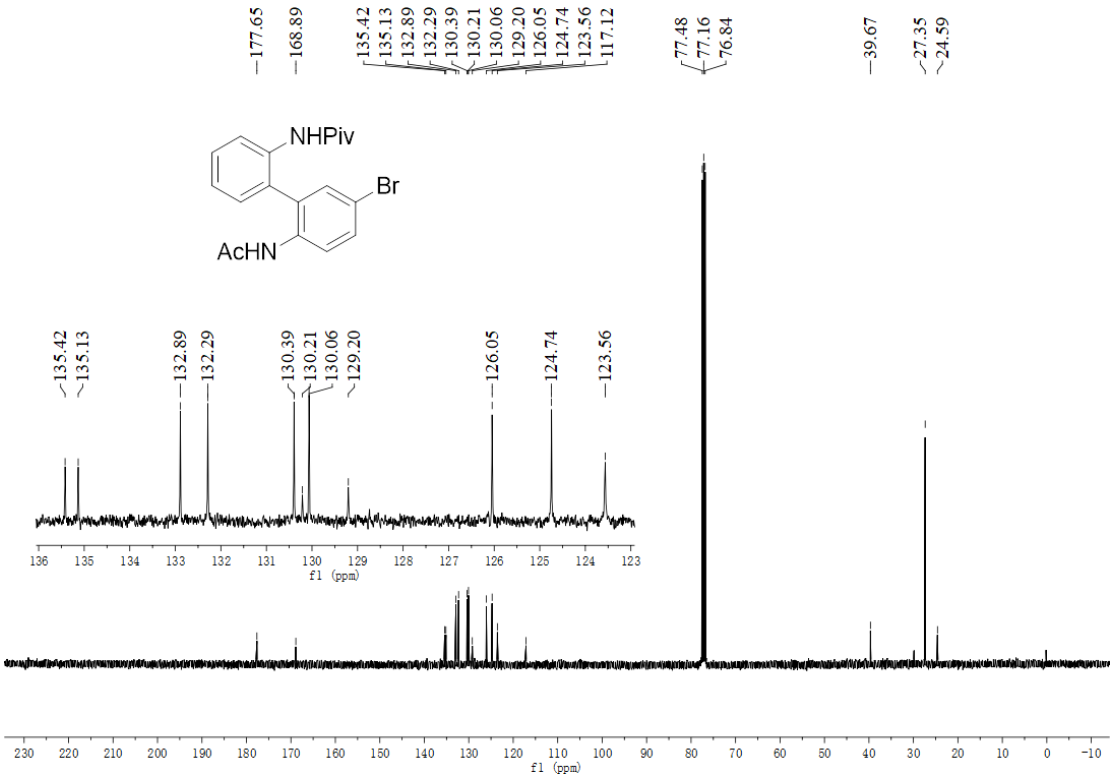
Ethyl 6-acetamido-2'-pivalamido-[1,1'-biphenyl]-3-carboxylate (4b)



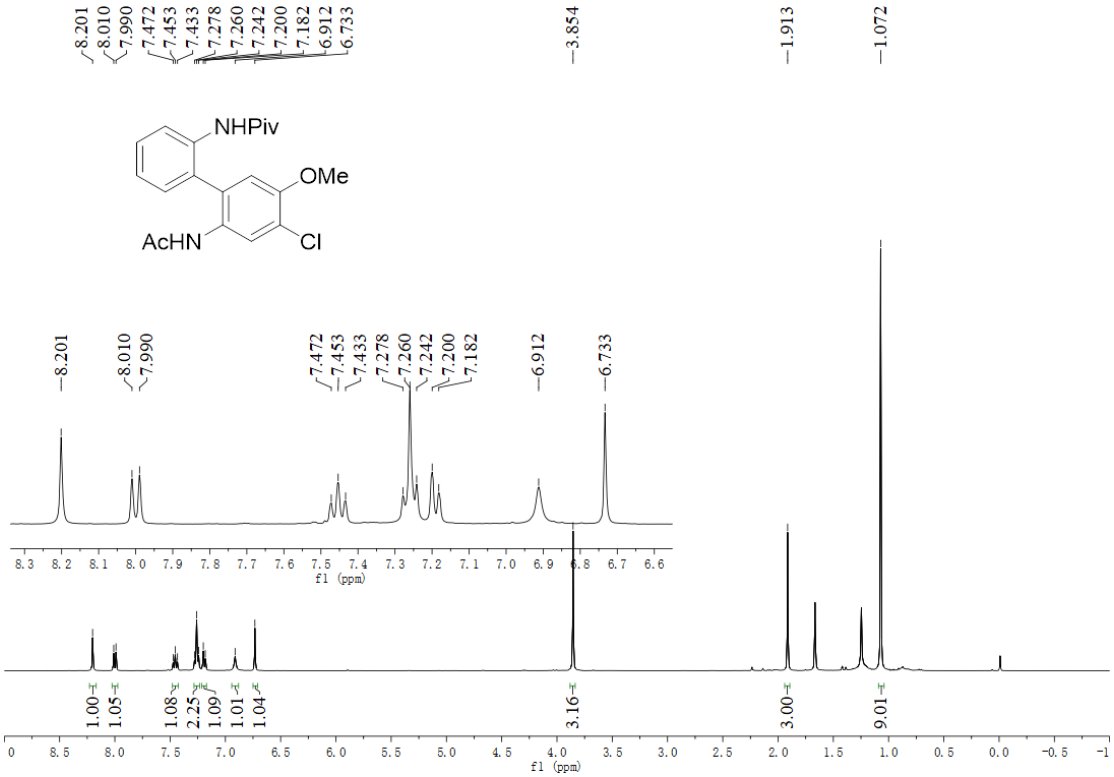


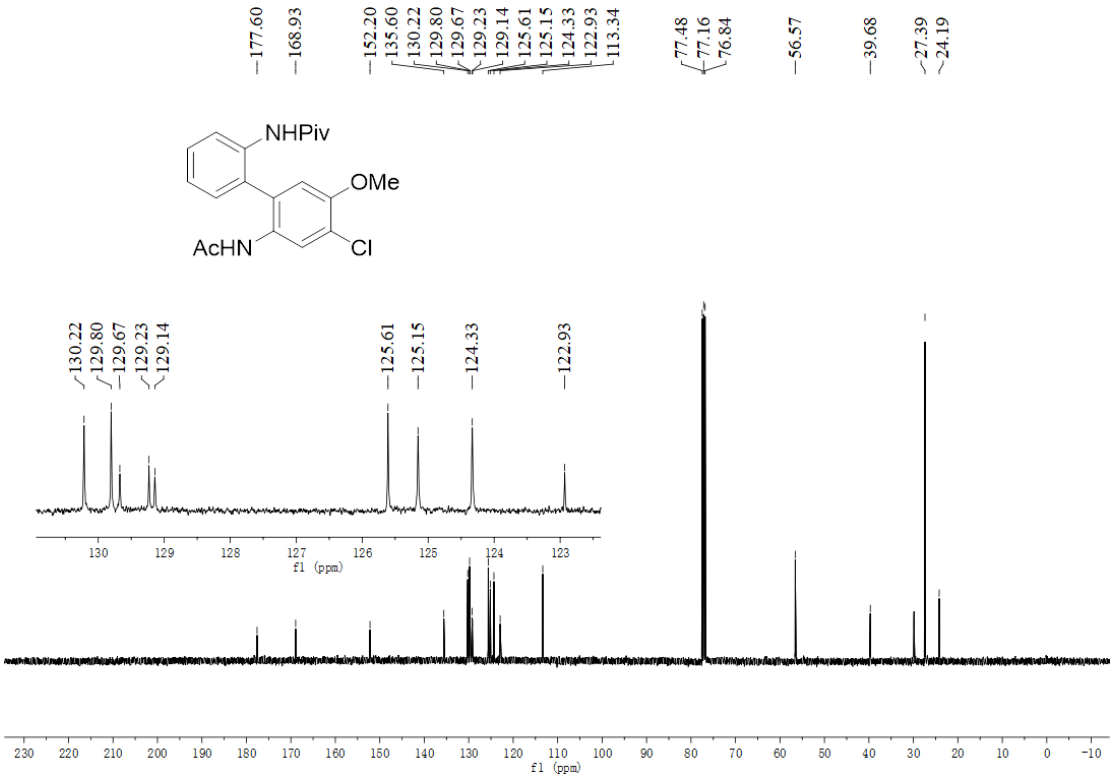
N-(2'-Acetamido-5'-bromo-[1,1'-biphenyl]-2-yl)pivalamide (4c)



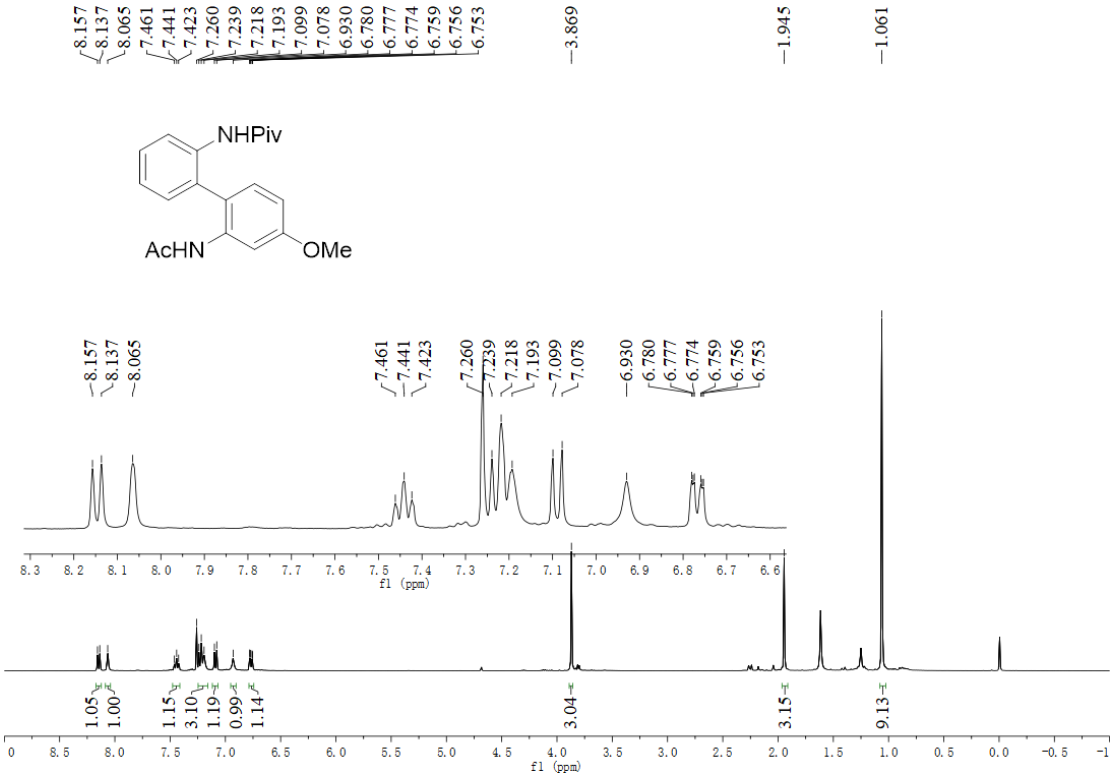


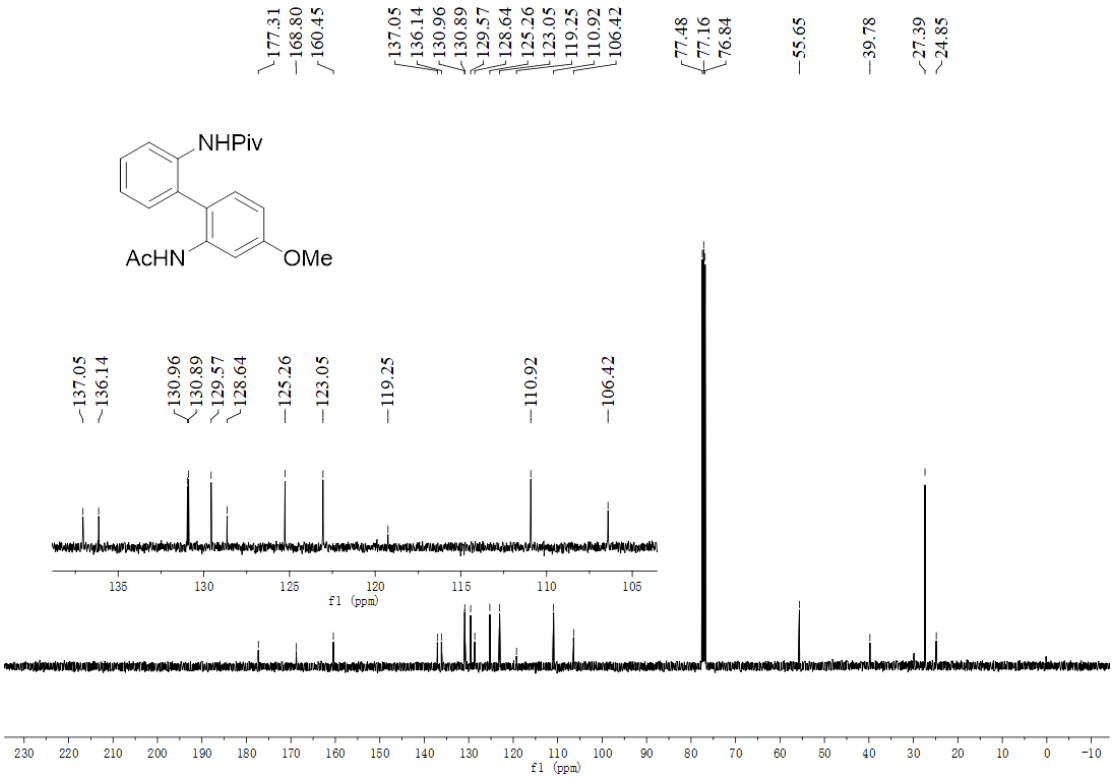
N-(2'-Acetamido-4'-chloro-5'-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (4d)



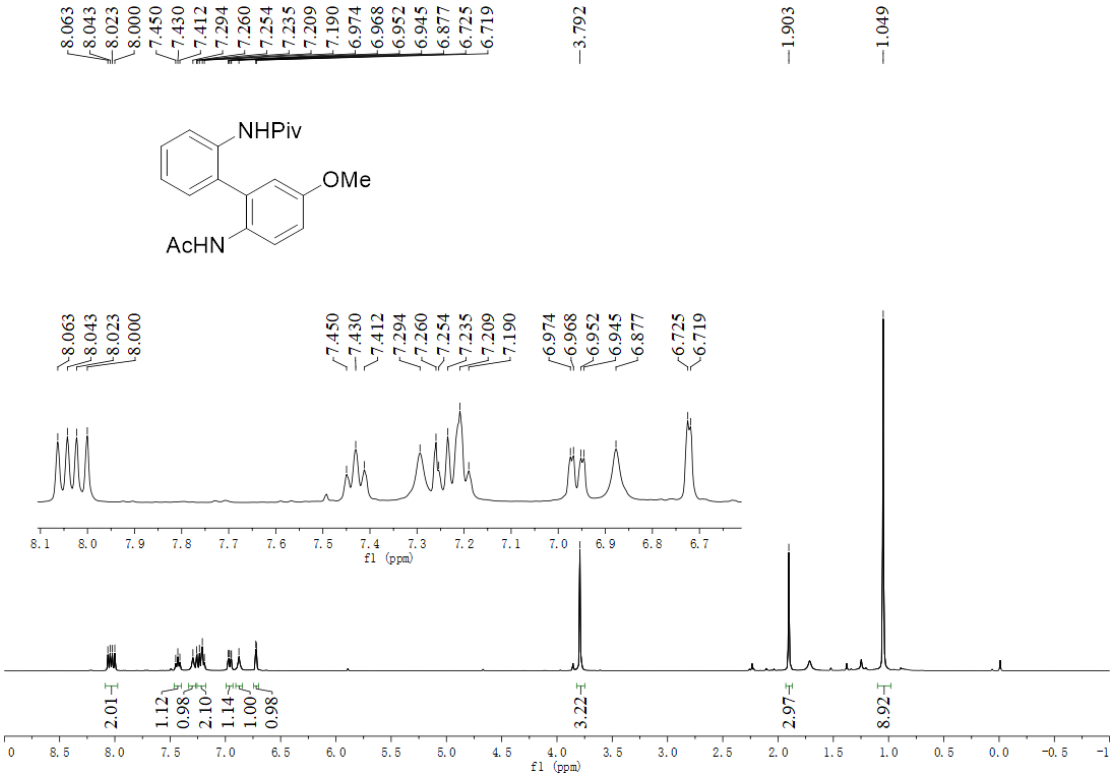


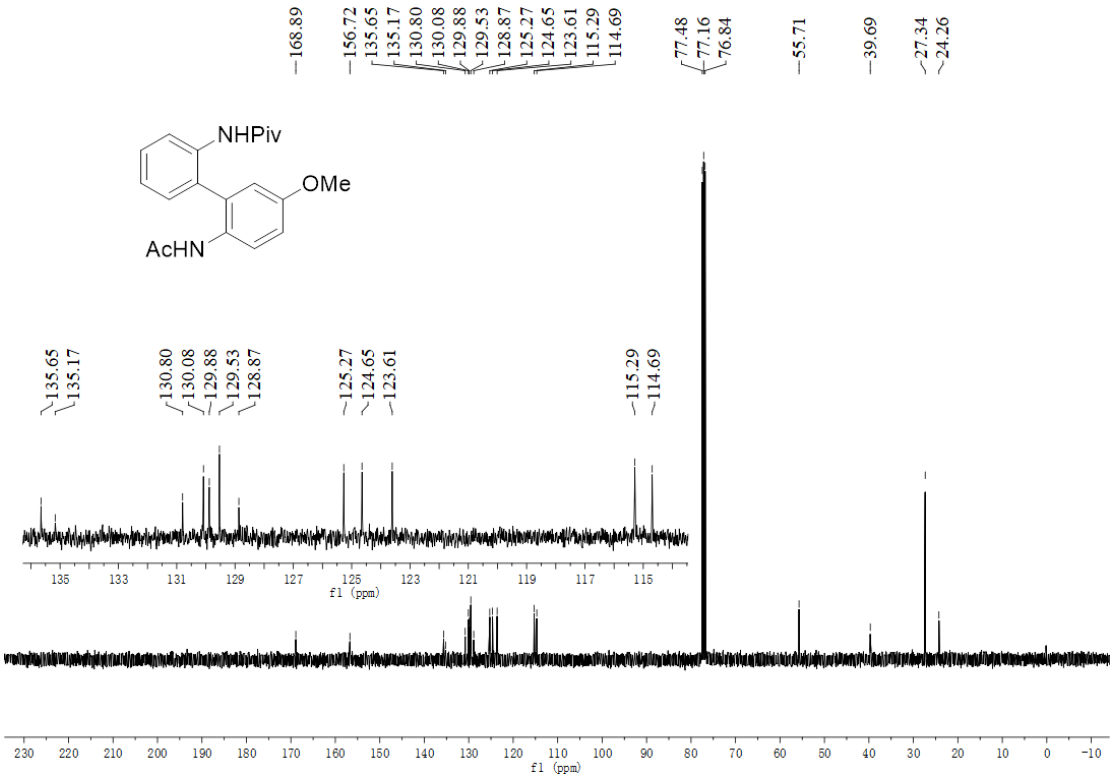
N-(2'-Acetamido-4'-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (4e)



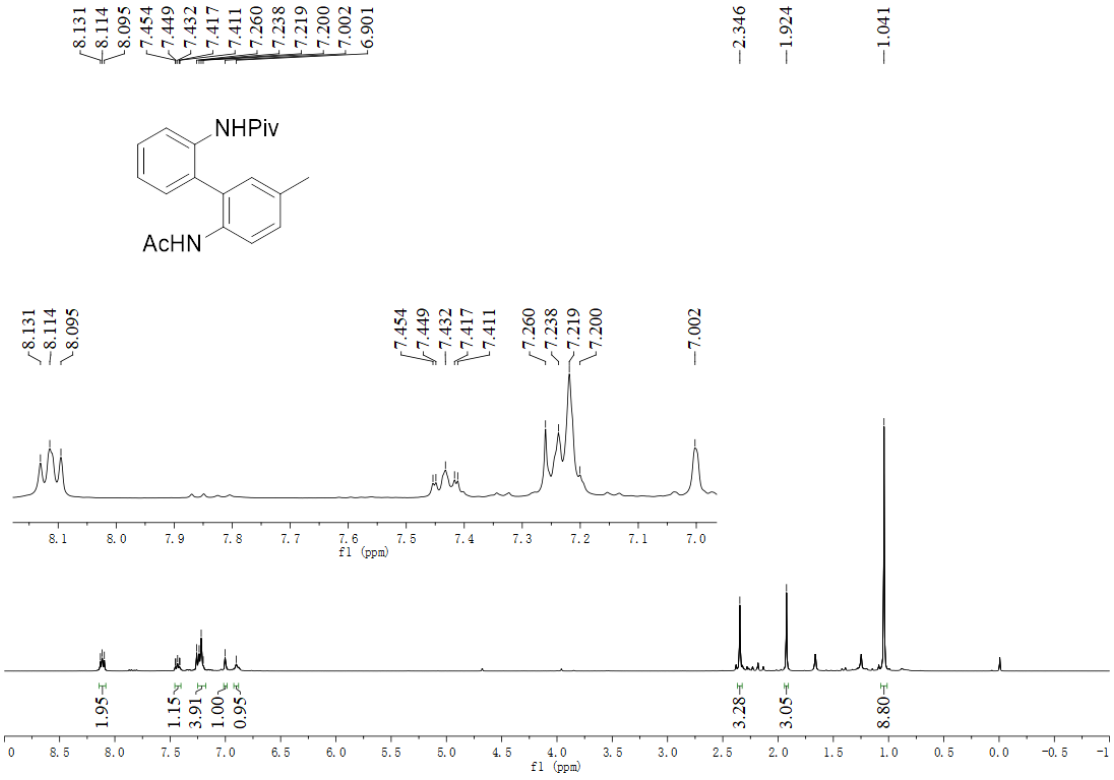


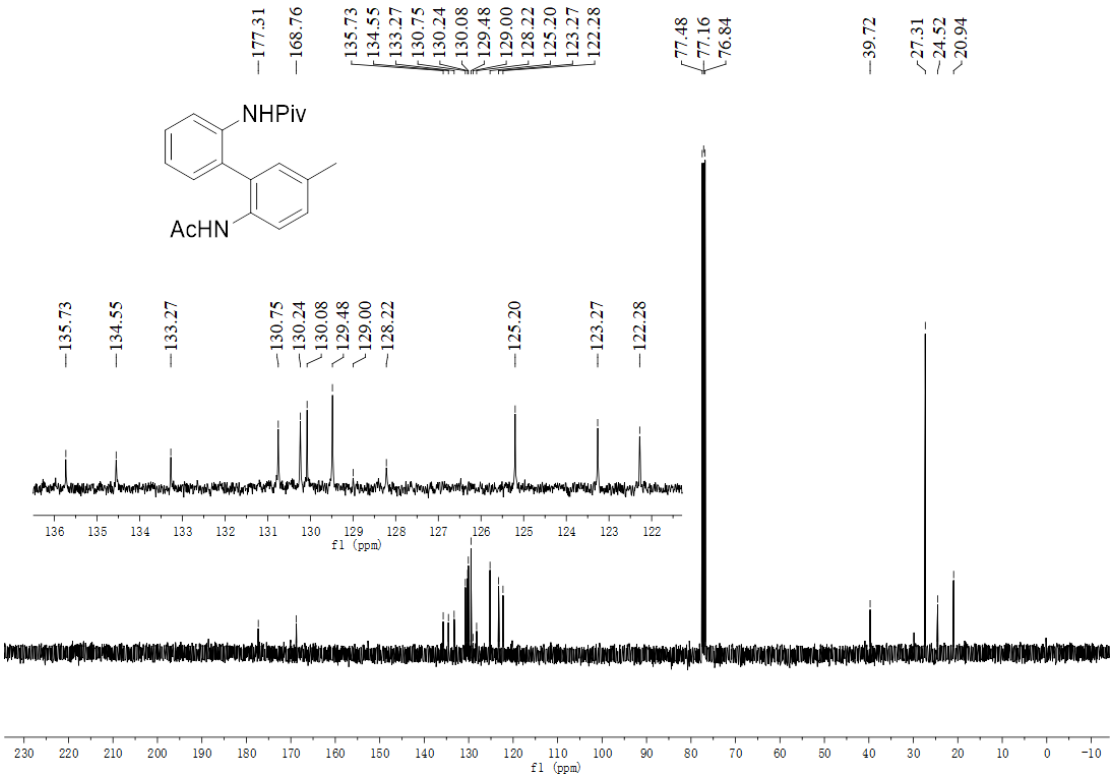
N-(2'-Acetamido-5'-methoxy-[1,1'-biphenyl]-2-yl)pivalamide (4f)



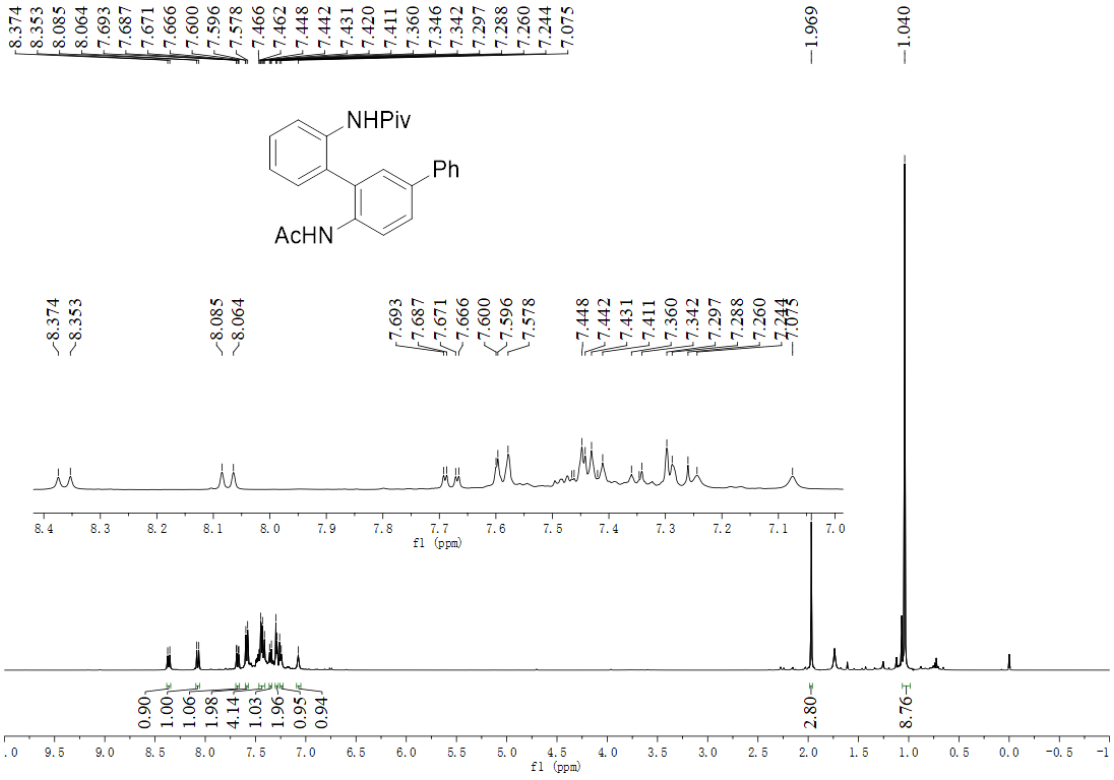


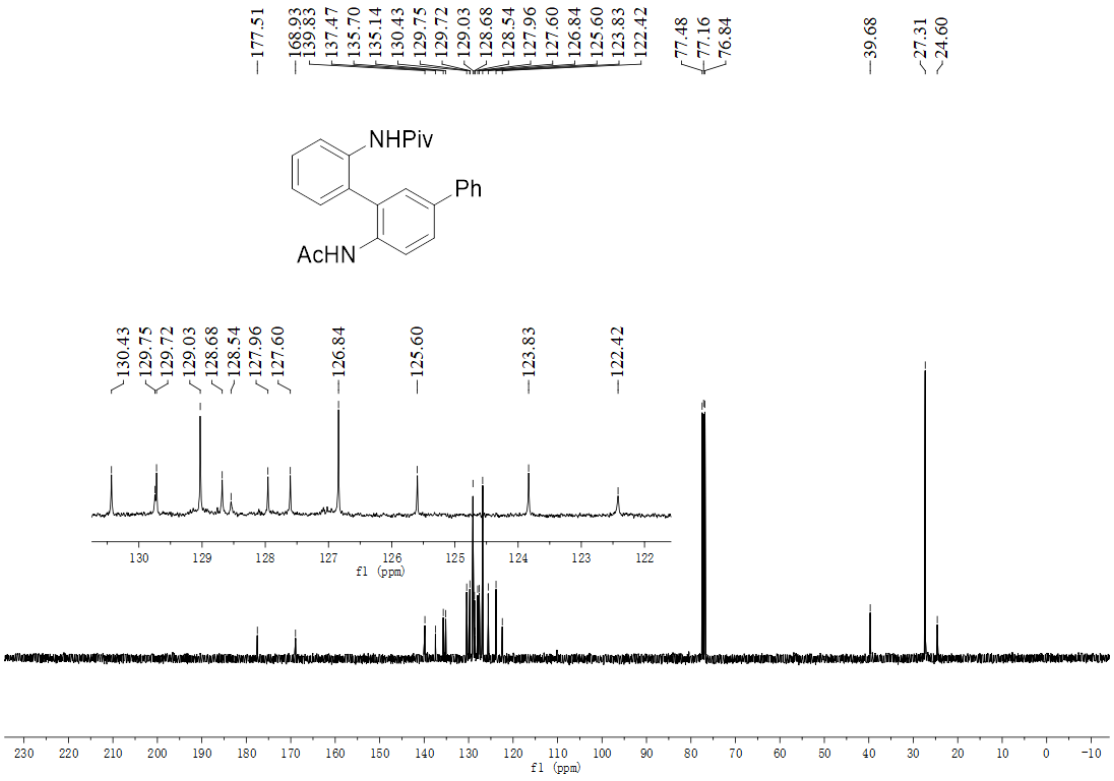
N-(2'-Acetamido-5'-methyl-[1,1'-biphenyl]-2-yl)pivalamide (4g)



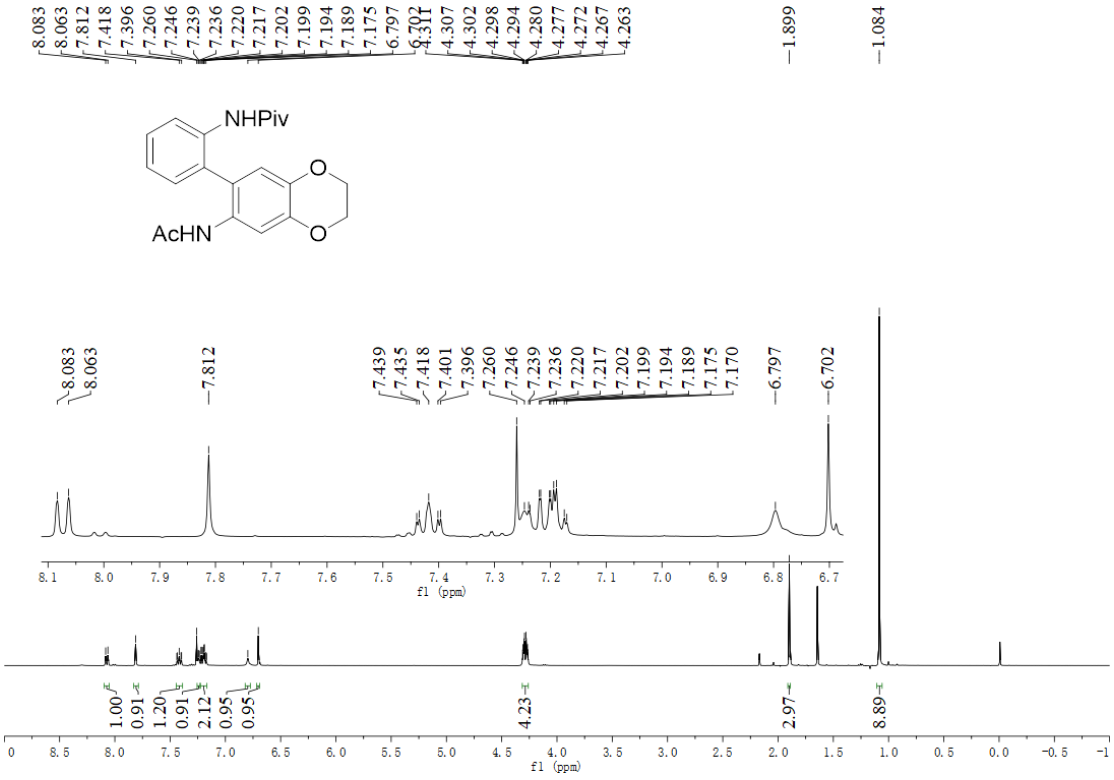


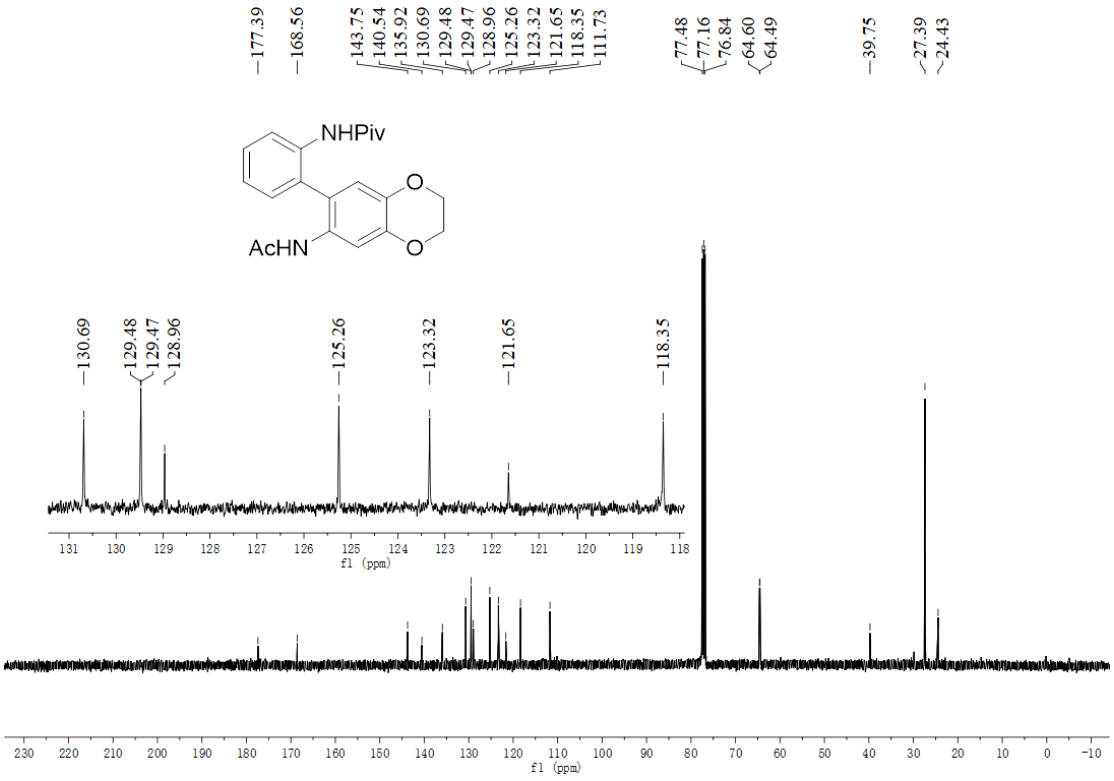
N-(6'-Acetamido-[1,1':3',1''-terphenyl]-2-yl)pivalamide (4h)



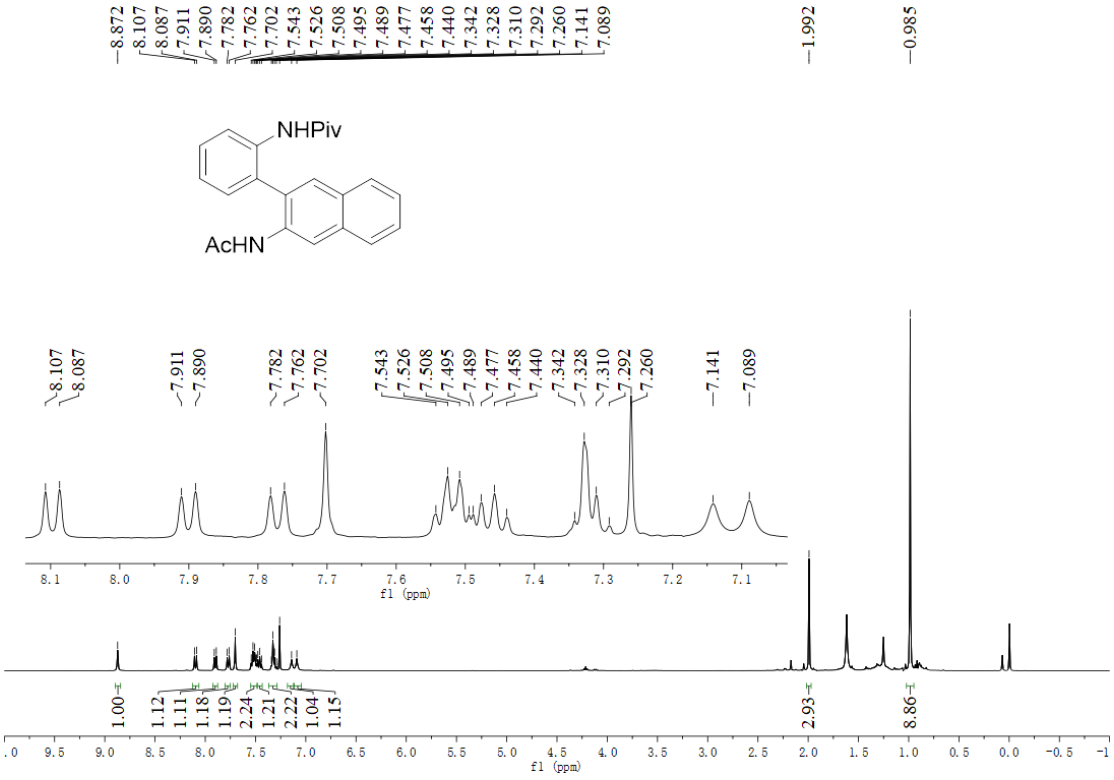


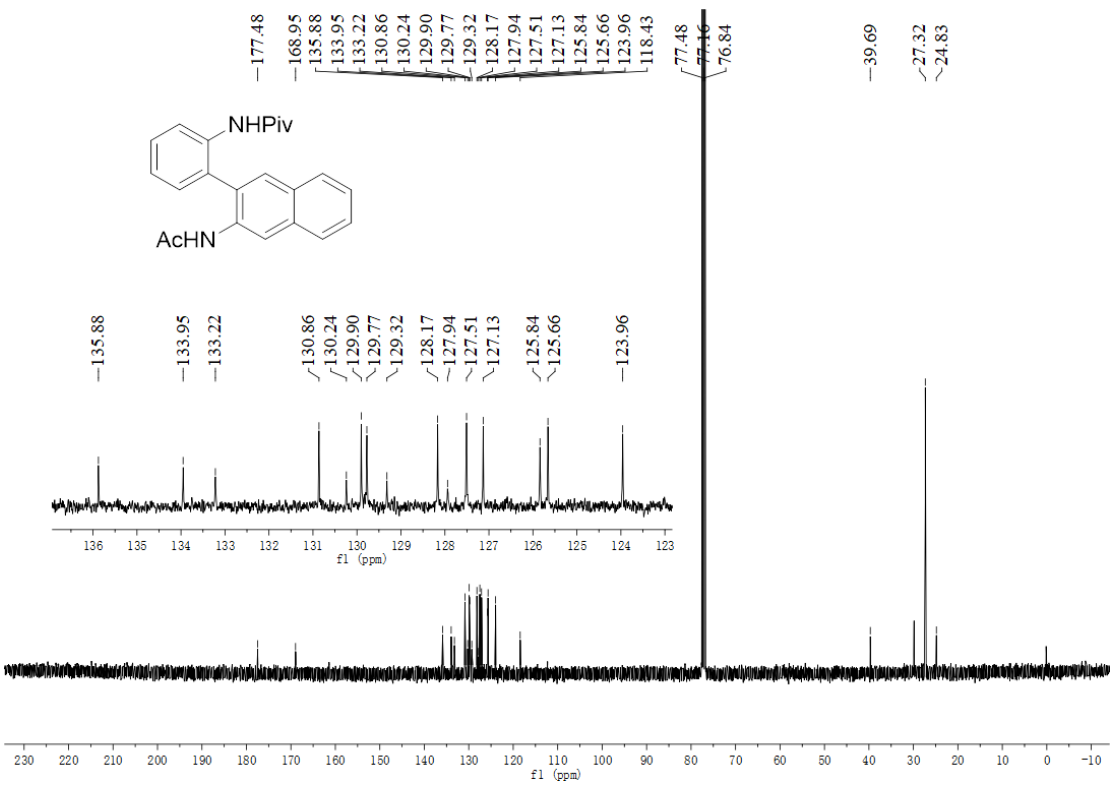
N-(2-(7-Acetamido-2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)phenyl)pivalamide (4i)



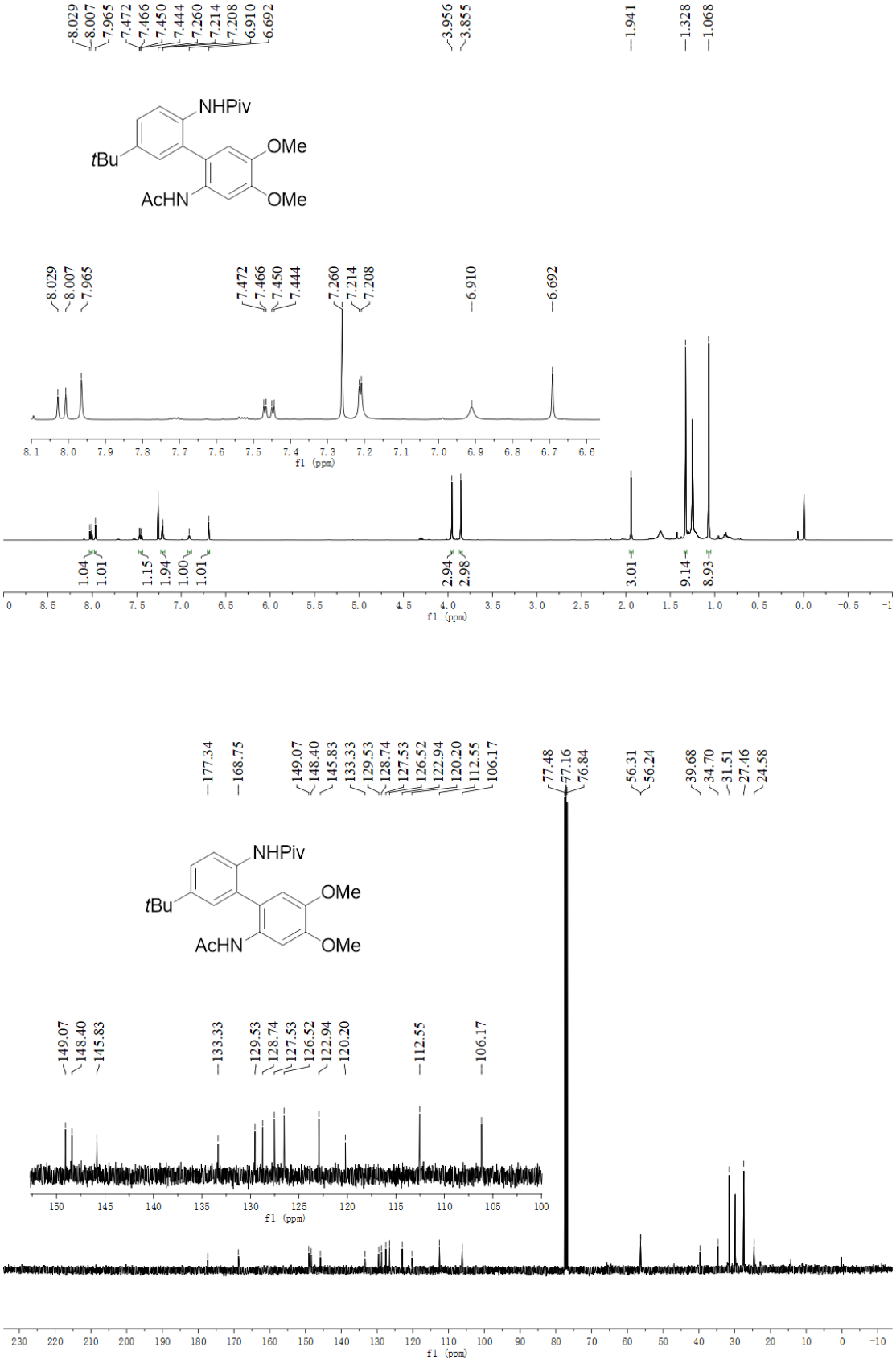


N-(2-(3-Acetamidonaphthalen-2-yl)phenyl)pivalamide (4j)

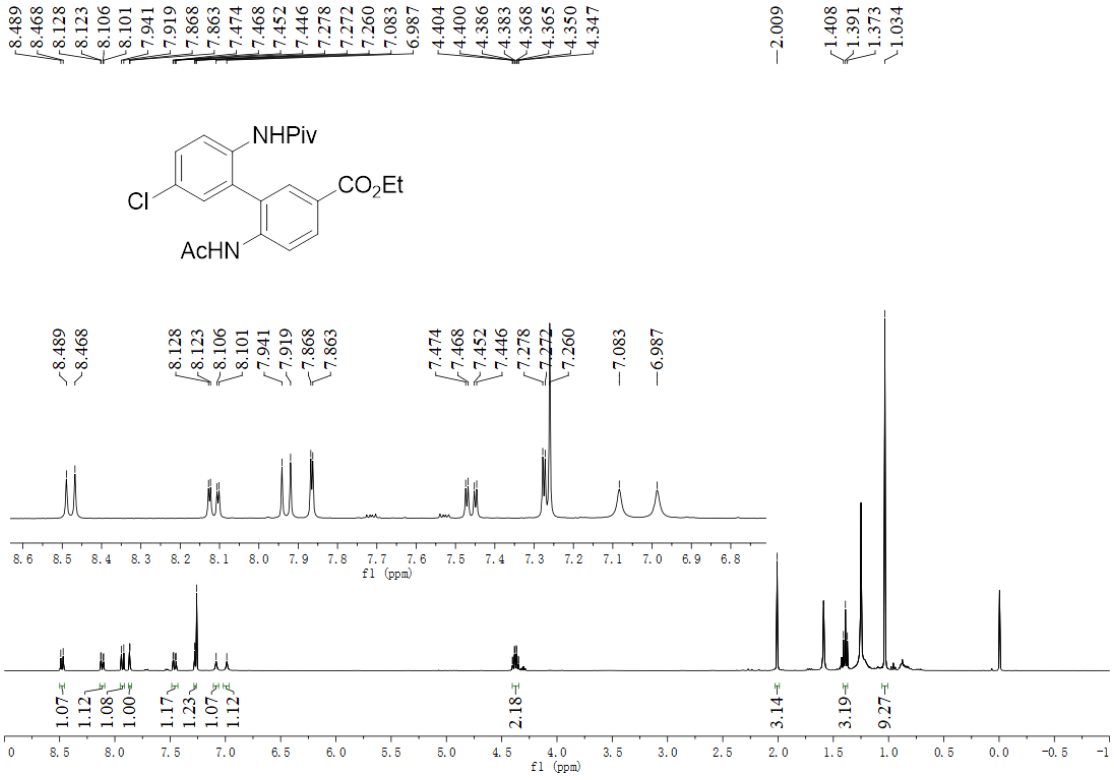


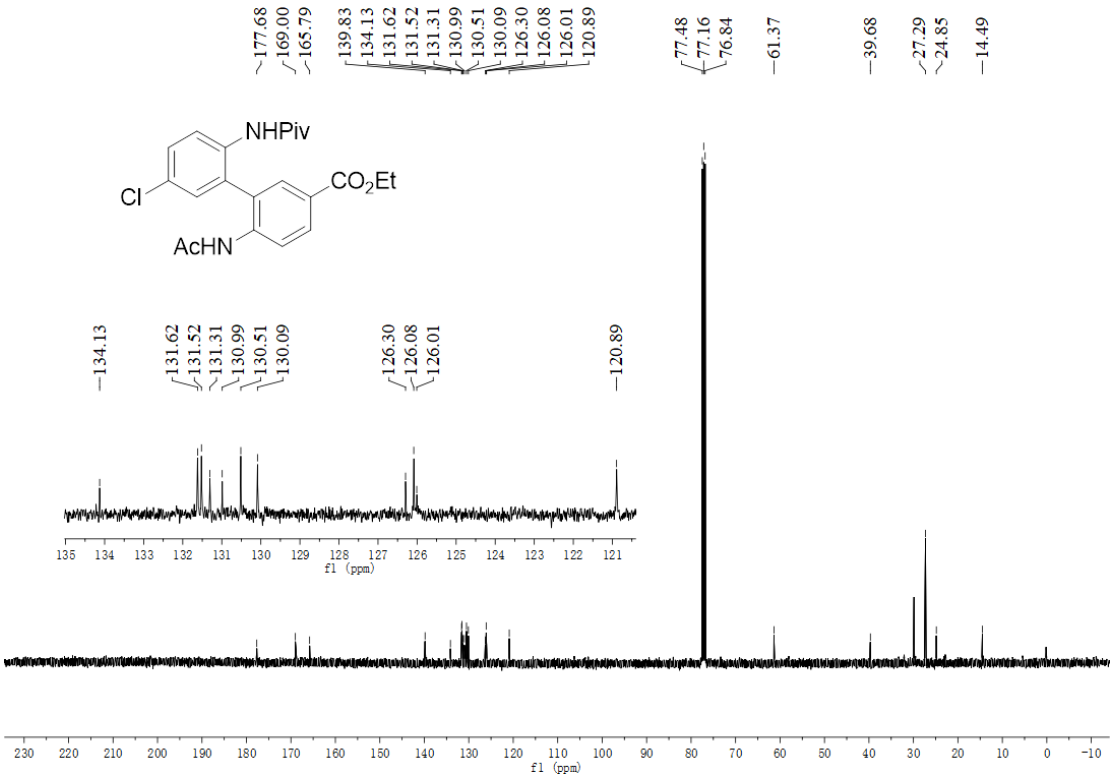


***N*-(2'-Acetamido-5-(*tert*-butyl)-4',5'-dimethoxy-[1,1'-biphenyl]-2-yl)pivalamide (4k)**

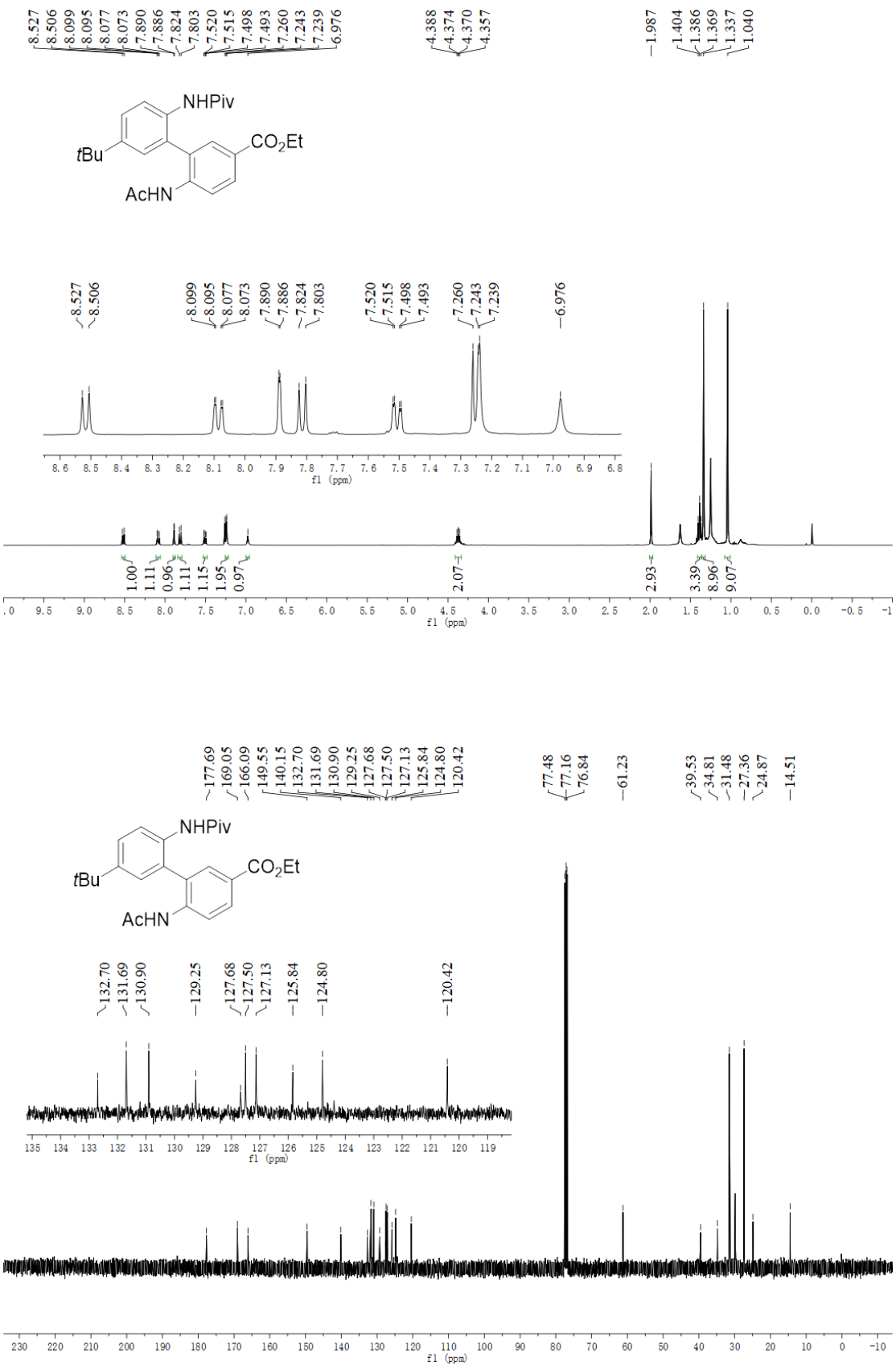


Ethyl 6-acetamido-5'-chloro-2'-pivalamido-[1,1'-biphenyl]-3-carboxylate (4l)

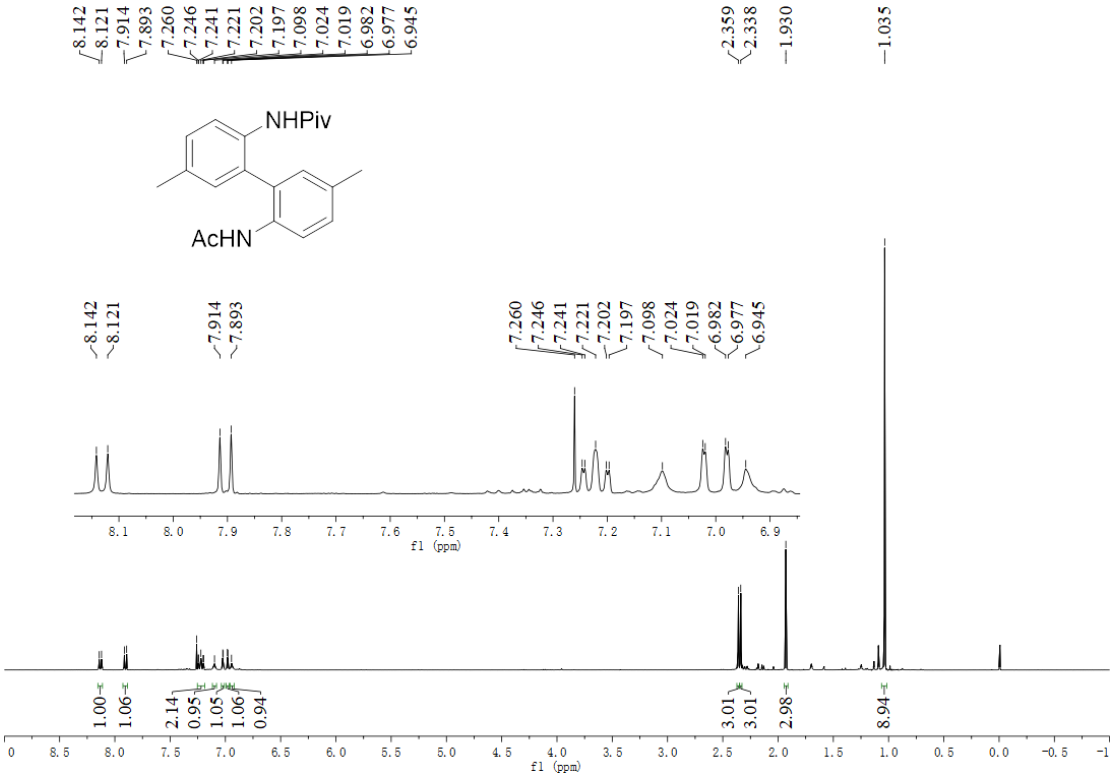


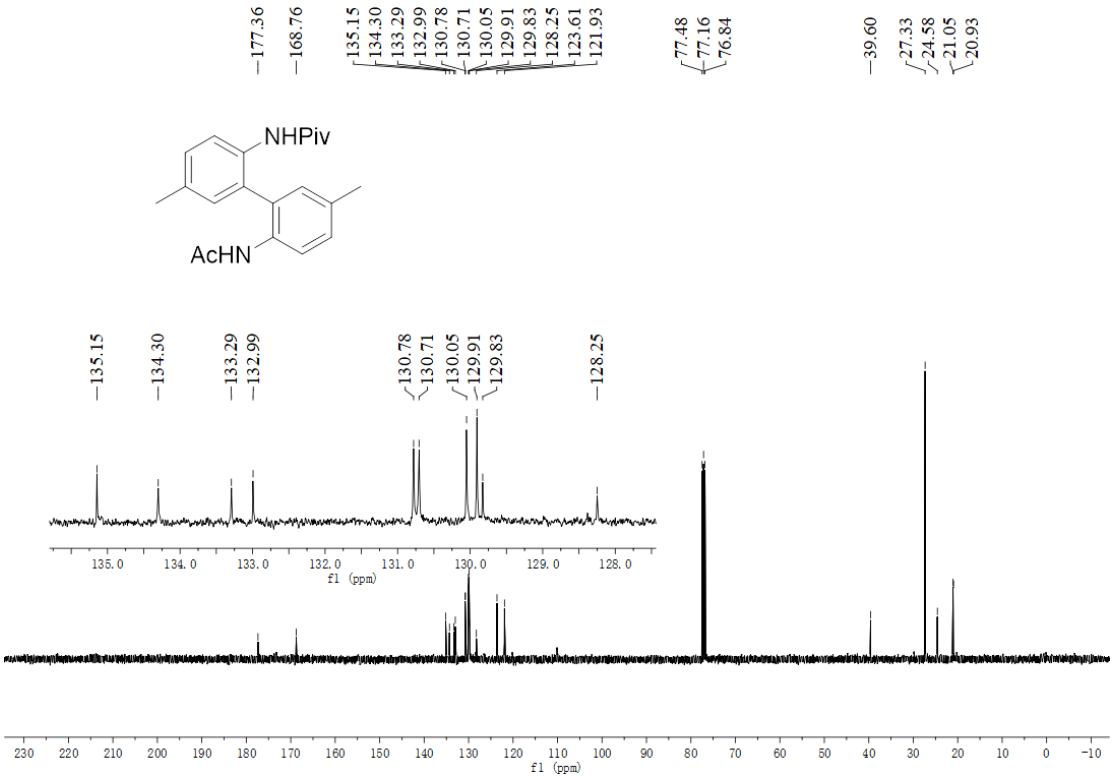


Ethyl 6-acetamido-5'-(*tert*-butyl)-2'-pivalamido-[1,1'-biphenyl]-3-carboxylate (4m)

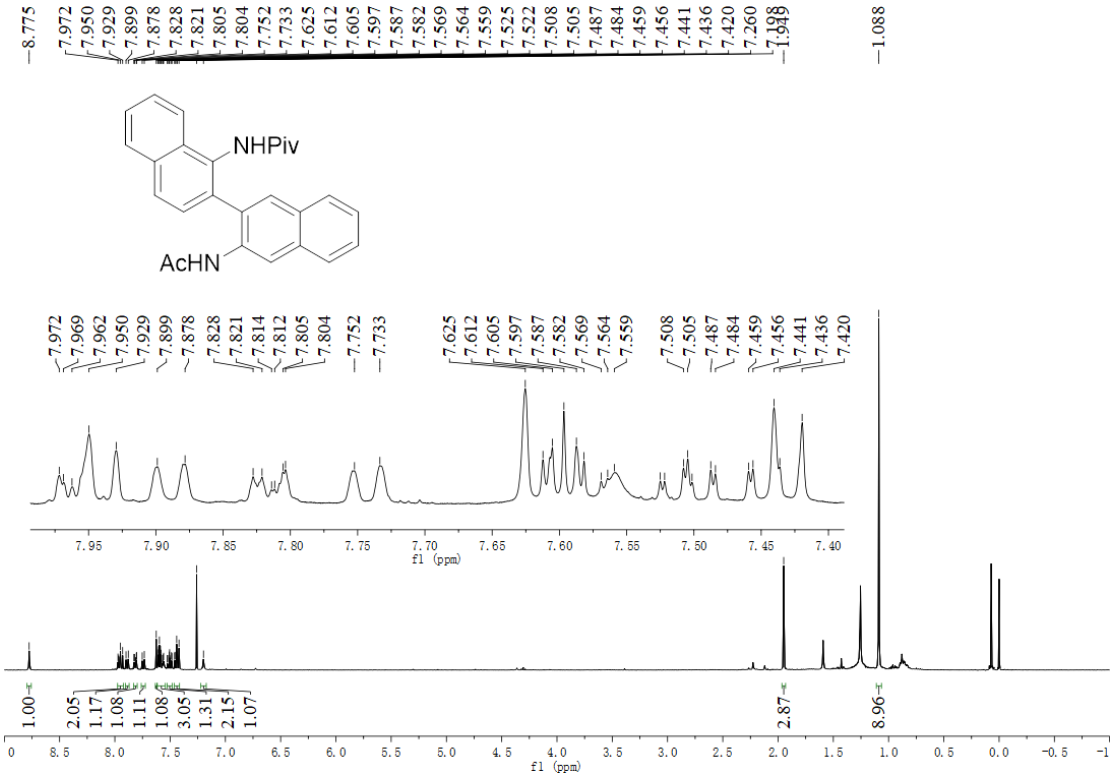


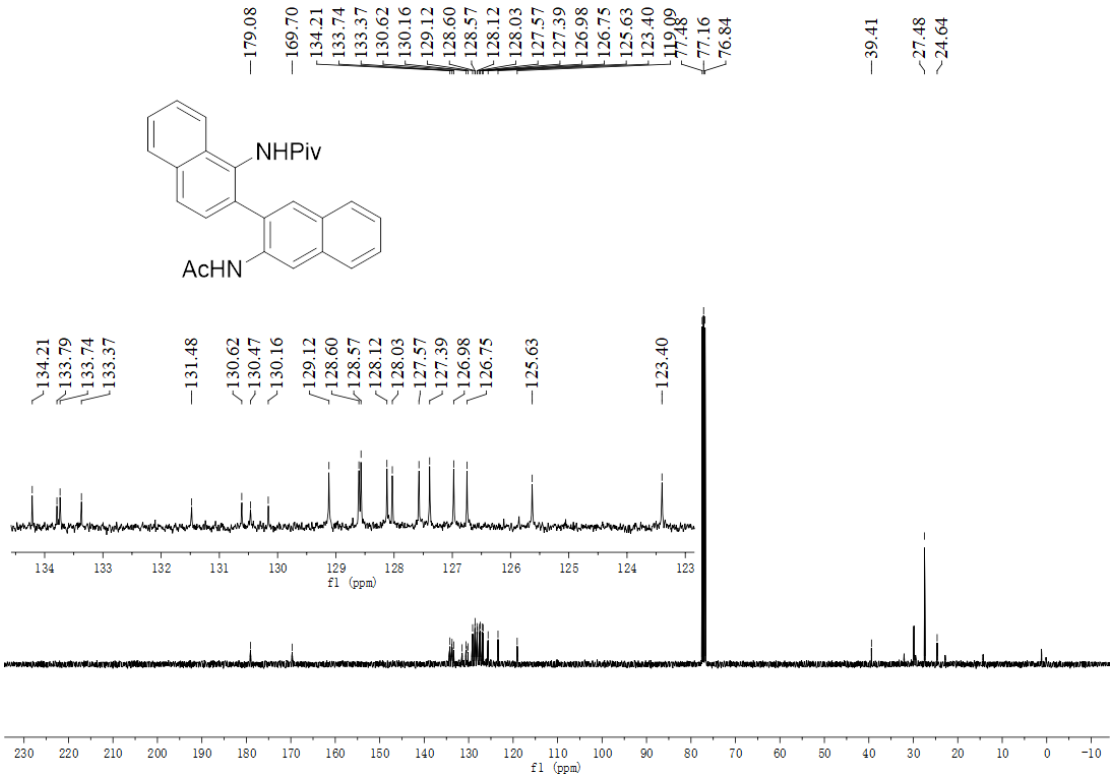
N-(2'-Acetamido-5,5'-dimethyl-[1,1'-biphenyl]-2-yl)pivalamide (4n)



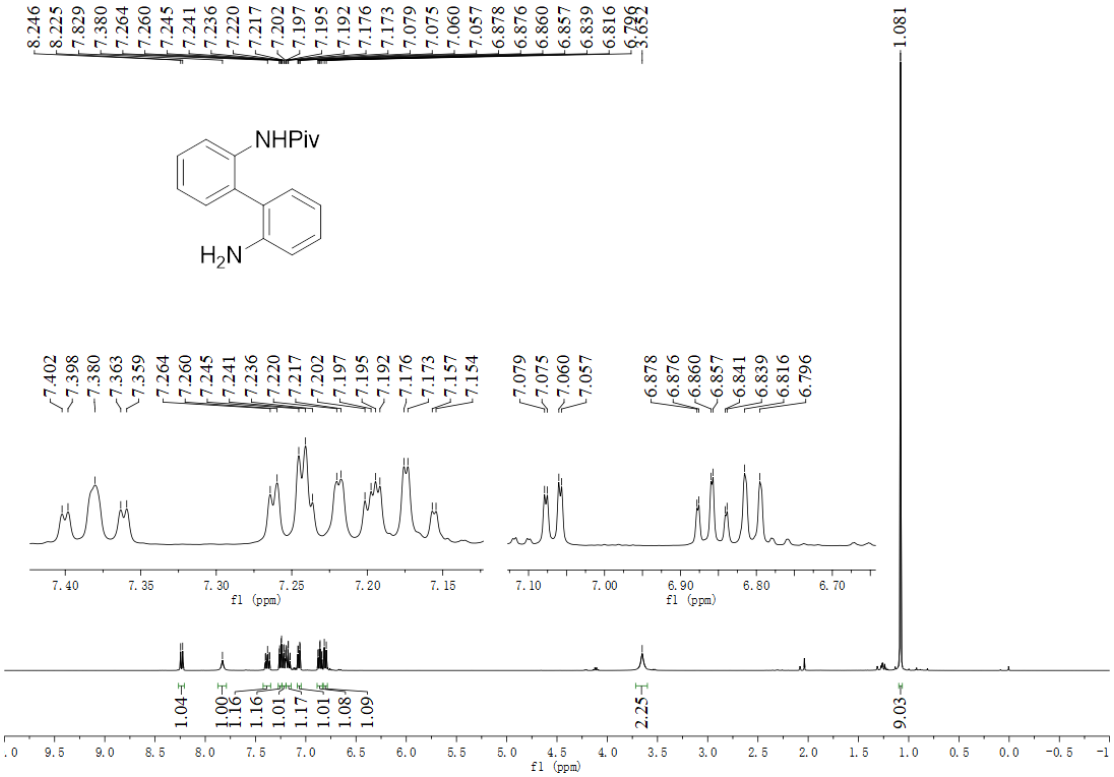


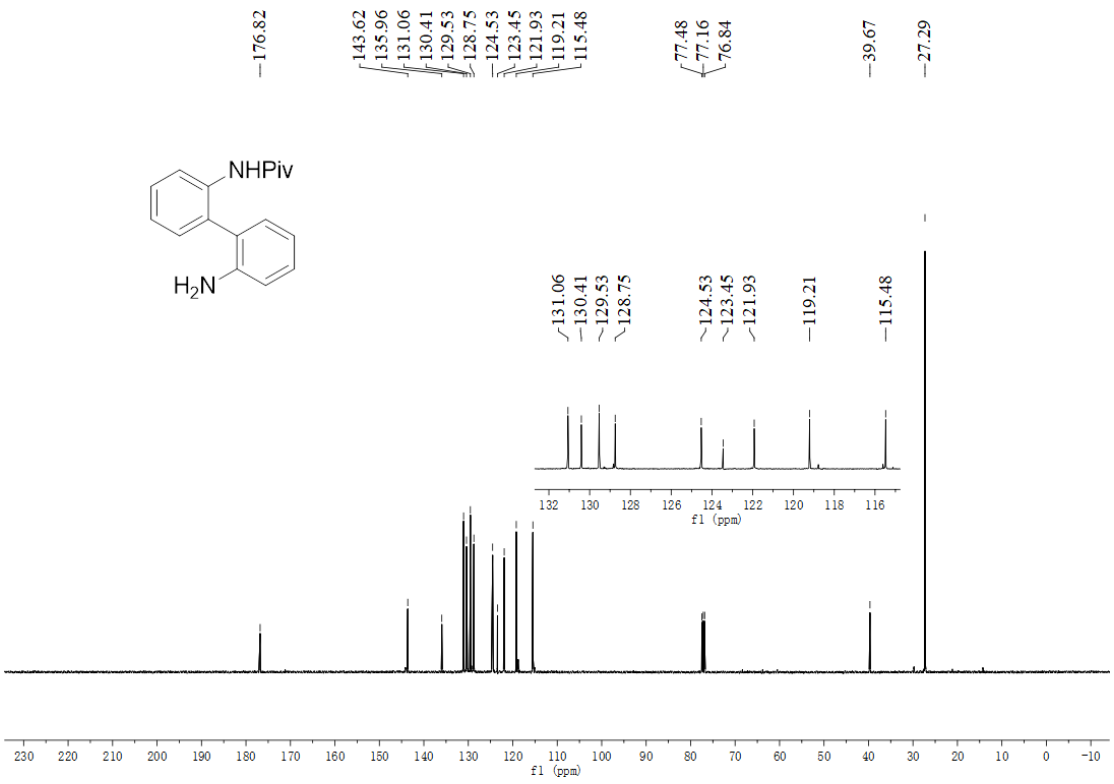
N-(3'-Acetamido-[2,2'-binaphthalen]-1-yl)pivalamide (4o)





N-(2'-Amino-[1,1'-biphenyl]-2-yl)pivalamide (5a)





[1,1'-Biphenyl]-2,2'-diamine (6a)