Supporting Information

Cp*Ir(III)-Catalyzed Mild and Broad C–H Arylation of Arenes and Alkenes with Aryldiazonium Salts Leading to the External Oxidant-Free Approach

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I. General Methods

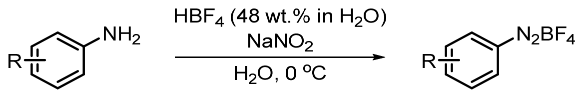
Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by UV light (254 nm). Silica-gel chromatography was performed using a CombiFlash® R_f ⁺ system with RediSep® R_f Silica columns (230 – 400 mesh) using a proper eluent system. ^{1}H NMR was recorded on Bruker Ascend 400 (400 MHz) or Agilent Technologies DD2 (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the residual solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz (Hz). ^{13}C NMR was obtained on Bruker Ascend 400 (100 MHz) or Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the residual solvent peak. ^{19}F NMR was recorded on Agilent Technologies DD2 (564 MHz). Infrared (IR) spectra were acquired on Bruker Alpha ATR FT-IR Spectrometer. Frequencies are given in wave numbers (cm^{-1}) and only selected peaks were reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method and from the KAIST Research Analysis Center by using ESI method. X-ray diffraction data was collected on a Bruker SMART APEX II coated with Paraton-*N* oil under a stream of N_2 (g) at 120 K. Melting point was measured with Buchi Melting Point M-565.

II. Procedures for the Preparation of Starting Materials

1. Preparation of Benzamides, Enamides and Quinoline *N*-Oxides

Benzamides,[S1] enamides,[S2] and quinoline *N*-oxides[S3] were prepared according to literature procedures.

2. Preparation of Aryldiazonium Tetrafluoroborates (2)[S4]

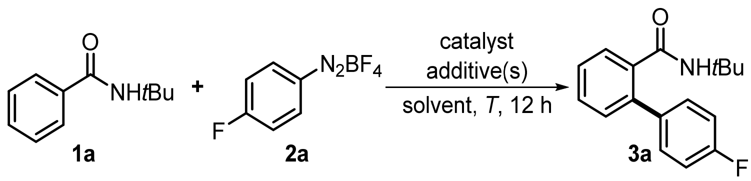


To a solution of aniline (10 mmol) in distilled water (6 mL) was added tetrafluoroboric acid solution (48 wt.% in H_2O, 3.4 mL, 26 mmol) at 0 °C. Sodium nitrite (0.7 g, 10 mmol) in distilled water (2 mL) was added dropwise and allowed to stir for 1 h at 0 °C. Thick precipitate was collected by filtration washing with diethyl ether (40 mL). The resulting precipitate was further purified by recrystallization with acetonitrile/diethyl ether to give desired aryldiazonium tetrafluorborate as a white solid.

III. Procedure for the Optimization Study (Table 1)

To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *N-tert*-butylbenzamide (**1a**, 26.6 mg, 0.15 mmol), 4-fluorophenyldiazonium tetrafluoroborate (**2a**, 21.0 mg, 0.1 mmol), catalyst, additive(s), and solvent (0.5 mL, 0.2 M) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at the indicated temperature for 12 h, filtered through a pad of silica with *n*-hexane/EtOAc (2:1, 10 mL x 4) and concentrated under reduced pressure. The crude yield was measured by using ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

Table S1. Optimization of the Ir-Catalyzed C–H Arylation Reaction[a]



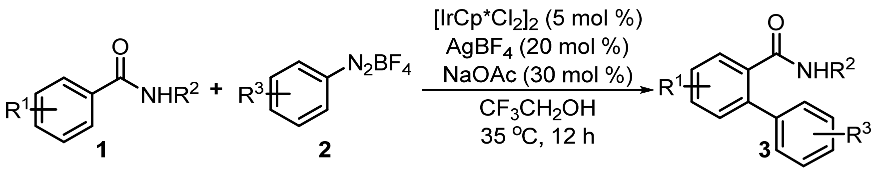
Entry	Catalyst (mol %)	Additive(s) (mol %)	Solvent	*T* (°C)	Yield (**3a**)[b]
1	$[RhCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	1,2-DCE	50	N.R.
2	[Ru(*p*-cyemene)Cl_2]$_2$ (5)	$AgNTf_2$ (20)	1,2-DCE	50	N.R.
3	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	1,2-DCE	50	55
4	$[IrCp^*Cl_2]_2$ (5)	-	1,2-DCE	50	N.R.
5	-	$AgNTf_2$ (20)	1,2-DCE	50	N.R.

6	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	CH_2Cl_2	50	40
7	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	1,1,2,2-TCE	50	N.R.
8	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	THF	50	N.R.
9	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	1,4-dioxane	50	N.R.
10	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	acetone	50	N.R.
11	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	DMF	50	N.R.
12	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	CH_3CN	50	N.R.
13	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	MeOH	50	N.R.
14	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	*t*AmylOH	50	12
15	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	HFIP	50	N.R.
16	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	CF_3CH_2OH	50	70
17	$[IrCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20)	CF_3CH_2OH	35	68
18	$[IrCp^*Cl_2]_2$ (5)	$AgSbF_6$ (20)	CF_3CH_2OH	35	69
19	$[IrCp^*Cl_2]_2$ (5)	$AgPF_6$ (20)	CF_3CH_2OH	35	66
20	$[IrCp^*Cl_2]_2$ (5)	AgOTf (20)	CF_3CH_2OH	35	42
21	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20)	CF_3CH_2OH	35	56
22[c]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20)	CF_3CH_2OH	35	55
23[c]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / NaOAc (30)	CF_3CH_2OH	35	83 (78)
24[c]	$[IrCp^*Cl_2]_2$ (5)	NaOAc (30)	CF_3CH_2OH	35	N.R.
25[c]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / LiOAc (30)	CF_3CH_2OH	35	70
26[c]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / CsOAc (30)	CF_3CH_2OH	35	57
27[c]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / CsF (30)	CF_3CH_2OH	35	72
28[c]	$[IrCp^*Cl_2]_2$ (2.5)	$AgBF_4$ (10) / NaOAc (15)	CF_3CH_2OH	35	73
29[d]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / NaOAc (30)	CF_3CH_2OH	35	60[e]
30[c,f]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / NaOAc (30)	CF_3CH_2OH	35	81
31[c,g]	$[IrCp^*Cl_2]_2$ (5)	$AgBF_4$ (20) / NaOAc (30)	CF_3CH_2OH	35	79

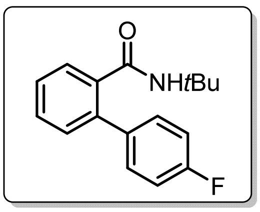
[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), catalyst, additive(s) and solvent (0.5 mL) at the indicated temperature for 12 h under argon atmosphere. Unless otherwise mentioned, **3a** was obtained exclusively and only trace (<5%) amount of **3a’** was produced. [b] NMR yields (%) are given and isolated yields are shown in parenthesis. [c] **1a** (0.3 mmol), **2a** (0.2 mmol) and solvent (1.0 mL) were used. [d] **1a** (0.2 mmol), **2a** (0.3 mmol) and solvent (1.0 mL) were used. [e] 7 % of **3a’** was produced. [f] Reaction under O_2 (1 atm.). [g] Reaction under dark.

IV. Procedures for the Ir-Catalyzed C–H Arylation with Aryldiazonium Tetrafloroborates

1. Procedure for the Ir-Catalyzed C–H Arylation of Benzamides with Aryldiazonium Tetrafluoroborates (Table 2 & Table 3)

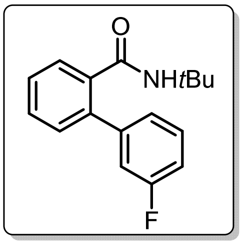


To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added benzamide (**1**, 0.3 mmol), aryldiazonium tetrafluoroborate (**2**, 0.2 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.01 mmol, 5 mol %), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol %), NaOAc (4.9 mg, 0.06 mmol, 30 mol %) and 2,2,2-trifluoroethanol (1.0 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 35 °C for 12 h, filtered through a pad of silica with *n*-hexane/EtOAc (2:1, 10 mL x 4) and concentrated under reduced pressure. The crude reaction mixture was further purified by silica gel column chromatography with *n*-hexane/EtOAc as an eluent to give the desired arylated product **3**.



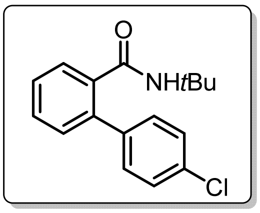
***N*-(*tert*-Butyl)-4'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3a**)

White solid; m.p. 129-130 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 8.4, 8.4 Hz, 2H), 5.05 (s, 1H), 1.16 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 162.5 (d, *J* = 239.4 Hz), 138.1, 137.0, 136.4 (d, *J* = 3.5 Hz), 130.5 (d, *J* = 8.2 Hz), 130.0, 129.7, 128.6, 127.7, 115.4 (d, *J* = 21.4 Hz), 51.4, 28.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.7 (m); IR (cm^{-1}) 3288, 2968, 2927, 1633, 1552, 1538, 1362, 1323, 1217, 1159, 839, 761; HRMS (EI) m/z calcd. for $C_{17}H_{18}FNO$ $[M]^+$: 271.1372, found: 271.1373.



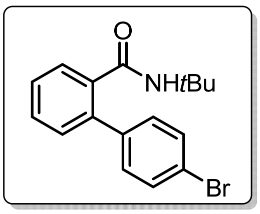
***N*-(*tert*-Butyl)-3'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3b**)

White solid; m.p. 97-98 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.15 (dt, *J* = 9.7, 2.1 Hz, 1H), 7.09 (td, *J* = 8.3, 2.3 Hz, 1H), 5.06 (s, 1H), 1.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 162.7 (d, *J* = 246.4 Hz), 142.6, 142.6, 138.0 (d, *J* = 1.7 Hz), 137.0, 130.1 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 3.1 Hz), 128.7, 128.0, 124.7 (d, *J* = 22.1 Hz), 115.9 (d, *J* = 21.7 Hz), 114.5 (d, *J* = 21.5 Hz), 51.5, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ –112.9 (m); IR (cm^{-1}) 3231, 3064, 2965, 1635, 1568, 1426, 1305, 1220, 1180, 1155, 870, 756; HRMS (EI) m/z calcd. for $C_{17}H_{18}FNO$ $[M]^+$: 271.1372, found: 271.1371.



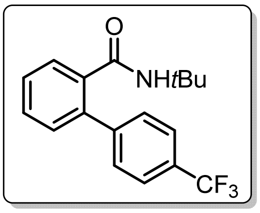
***N*-(*tert*-Butyl)-4'-chloro-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3c**)

White solid; m.p. 144-145 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.40 – 7.38 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 5.08 (s, 1H), 1.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 138.8, 138.0, 137.0, 133.8, 130.2, 129.8, 129.8, 128.6, 128.6, 127.8, 51.5, 28.3; IR (cm^{-1}) 3272, 2965, 2923, 1634, 1551, 1476, 1329, 1226, 1088, 1017, 833, 770; HRMS (EI) m/z calcd. for $C_{17}H_{18}ClNO$ $[M]^+$: 287.1077, found: 287.1076.



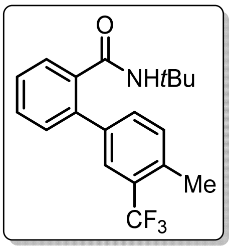
***N*-(*tert*-Butyl)-4'-bromo-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3d**)

White solid; m.p. 152-153 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.7 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.44 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 (m, 3H), 5.09 (s, 1H), 1.18 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 139.3, 138.0, 137.0, 131.5, 130.5, 129.8, 128.6, 127.8, 121.9, 51.5, 28.3; IR (cm^{-1}) 3288, 3080, 1634, 1548, 1444, 1360, 1327, 1224, 1071, 1043, 830, 756; HRMS (EI) m/z calcd. for $C_{17}H_{18}BrNO$ $[M]^+$: 331.0572, found: 331.0572.



***N*-(*tert*-Butyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3e**)

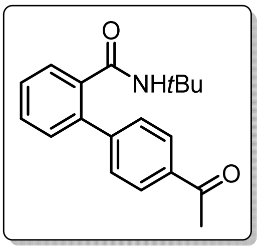
White solid; m.p. 149-150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 5.07 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 144.1, 137.9, 137.2, 129.9, 129.8, 129.8 (q, *J* = 33.0 Hz), 129.2, 128.5, 128.2, 125.3 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 273.4 Hz), 51.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.6 (s); IR (cm^{-1}) 3306, 2970, 1637, 1543, 1322, 1224, 1152, 1123, 1111, 1068, 846, 786; HRMS (EI) m/z calcd. for $C_{18}H_{18}F_3NO$ $[M]^+$: 321.1340, found: 321.1339.



***N*-(*tert*-Butyl)- 4'-methyl-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3f**)

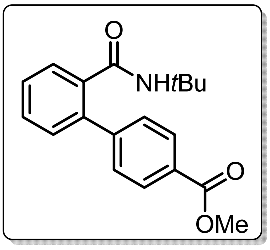
White solid; m.p. 116-117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 5.13 (s, 1H), 2.53 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 138.2, 138.0, 137.1, 136.0, 132.1, 131.9, 130.0, 129.9, 129.1 (q, *J* = 28.5 Hz), 128.5, 127.9, 126.1 (q, *J* = 4.4 Hz), 124.4 (q, *J* = 275.4 Hz), 51.5, 28.3, 19.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ –61.7

(s); IR (cm^{-1}) 3290, 2973, 1642, 1542, 1454, 1325, 1286, 1250, 1214, 1118, 1054, 1026; HRMS (EI) m/z calcd. for $C_{19}H_{20}F_3NO$ $[M]^+$: 335.1497, found: 335.1494.



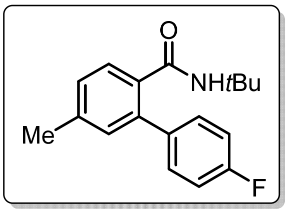
***N*-(*tert*-Butyl)-4'-acetyl-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3g**)

White solid; m.p. 136-137 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 1H), 2.64 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.6, 168.2, 145.2, 138.2, 137.1, 136.1, 129.8, 129.8, 129.0, 128.4, 128.4, 128.1, 51.5, 28.2, 26.6; IR (cm^{-1}) 3292, 2973, 1680, 1633, 1552, 1537, 1358, 1290, 1222, 1186, 844, 760; HRMS (EI) m/z calcd. for $C_{19}H_{21}NO_2$ $[M]^+$: 295.1572, found: 295.1570.



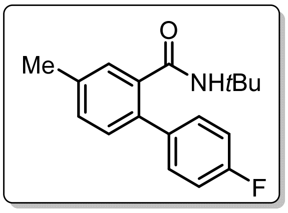
***N*-(*tert*-Butyl)-4'-methoxycarbonyl-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3h**)

White solid; m.p. 137-138 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 (td, *J* = 7.6, 1.4 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.10 (s, 1H), 3.94 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 166.7, 145.1, 138.2, 137.1, 129.8, 129.8, 129.7, 129.2, 128.9, 128.6, 128.1, 52.1, 51.5, 28.2; IR (cm^{-1}) 3282, 2994, 1720, 1626, 1550, 1435, 1389, 1327, 1281, 1104, 859, 750; HRMS (EI) m/z calcd. for $C_{19}H_{21}NO_3$ $[M]^+$: 311.1521, found: 311.1518.



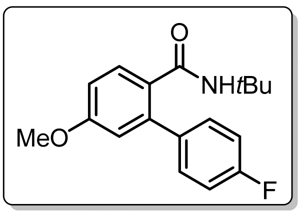
***N*-(*tert*-Butyl)-4'-fluoro-5-methyl-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3i**)

White solid; m.p. 131-132 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.13 – 7.10 (m, 3H), 5.00 (s, 1H), 2.39 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 162.5 (d, *J* = 246.3 Hz), 139.9, 138.2, 136.6 (d, *J* = 3.5 Hz), 134.2, 130.6, 130.5 (d, *J* = 7.9 Hz), 128.8, 128.4, 115.4 (d, *J* = 22.6 Hz), 51.3, 28.3, 21.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.8 (m); IR (cm^{-1}) 3263, 2965, 1647, 1610, 1547, 1514, 1453, 1360, 1324, 1220, 1122, 827; HRMS (EI) m/z calcd. for $C_{18}H_{20}FNO$ $[M]^+$: 285.1529, found: 285.1530.



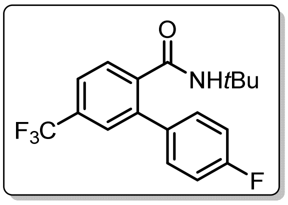
***N*-(*tert*-Butyl)-4'-fluoro-4-methyl-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3j**)

White solid; m.p. 131-132 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.37 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 8.6, 8.6 Hz, 2H), 5.02 (s, 1H), 2.40 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 162.4 (d, *J* = 246.5 Hz), 137.6, 136.8, 136.4 (d, *J* = 3.5 Hz), 135.3, 130.6, 130.5 (d, *J* = 4.0 Hz), 129.9, 129.2, 115.3 (d, *J* = 21.3 Hz), 51.4, 28.3, 20.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ –115.0 (m); IR (cm^{-1}) 3293, 2964, 1633, 1549, 1486, 1477, 1361, 1321, 1217, 1159, 1094, 823; HRMS (EI) m/z calcd. for $C_{18}H_{20}FNO$ $[M]^+$: 285.1529, found: 285.1525.



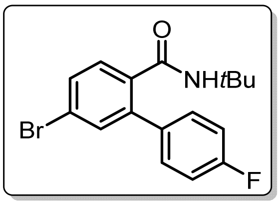
***N*-(*tert*-Butyl)-4'-fluoro-5-methoxy-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3k**)

Beige solid; m.p. 113-114 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.13 (dd, *J* = 8.6, 8.6 Hz, 2H), 6.92 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 4.96 (s, 1H), 3.84 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8, 162.6 (d, *J* = 244.8 Hz), 160.4, 140.0, 136.5 (d, *J* = 3.5 Hz), 130.8, 130.5 (d, *J* = 8.1 Hz), 129.4, 115.5, 115.4, 113.0, 55.4, 51.3, 28.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.3 (m); IR (cm^{-1}) 3289, 2994, 1634, 1609, 1566, 1518, 1488, 1453, 1313, 1294, 1215, 829; HRMS (EI) m/z calcd. for $C_{18}H_{20}FNO_2$ $[M]^+$: 301.1478, found: 301.1476.



***N*-(*tert*-Butyl)-4'-fluoro-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3l**)

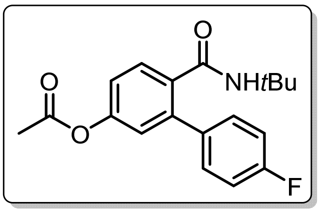
White solid; m.p. 139-140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.58 (s, 1H), 7.42 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.16 (dd, *J* = 8.6, 8.6 Hz, 2H), 5.07 (s, 1H), 1.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.1, 162.9 (d, *J* = 254.3 Hz), 140.2, 138.8, 134.9 (d, *J* = 3.4 Hz), 131.8 (q, *J* = 32.5 Hz), 130.5 (d, *J* = 8.4 Hz), 129.2, 126.9 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 275.5 Hz), 115.8 (d, *J* = 21.9 Hz), 51.8, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.9 (s), –113.3 (m); IR (cm^{-1}) 3283, 2974, 1663, 1545, 1513, 1325, 1223, 1175, 1128, 1072, 1030, 885; HRMS (EI) m/z calcd. for $C_{18}H_{17}F_4NO$ $[M]^+$: 339.1246, found: 339.1244.



***N*-(*tert*-Butyl)-4'-fluoro-5-bromo-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3m**)

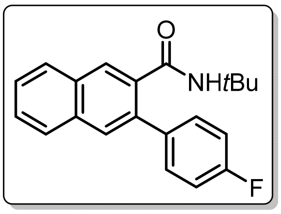
White solid; m.p. 143-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.52 (m, 2H), 7.47 (s, 1H), 7.38 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.13 (dd, *J* = 8.6, 8.6 Hz, 2H), 5.03 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 162.6 (d, *J* = 248.7 Hz), 140.0, 135.80, 135.0 (d, *J* = 3.5 Hz), 132.7, 130.7, 130.5 (d, *J* = 8.5 Hz), 130.3, 123.8, 115.6 (d, *J* = 24.2 Hz), 51.6, 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ

–113.5 (m); IR (cm^{-1}) 3254, 2963, 1637, 1556, 1510, 1468, 1323, 1221, 1158, 1024, 878, 834; HRMS (EI) m/z calcd. for $C_{17}H_{17}BrFNO$ $[M]^+$: 349.0478, found: 349.0475.



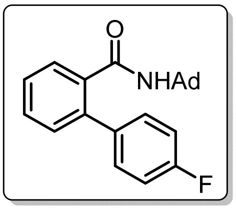
***N*-(*tert*-Butyl)-4'-fluoro-5-acetoxy-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3n**)

White solid; m.p. 128-129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 8.4, 5.5 Hz, 2H), 7.13 – 7.10 (m, 3H), 7.05 (d, J = 2.3 Hz, 1H), 5.06 (s, 1H), 2.31 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 167.5, 162.7 (d, J = 245.1 Hz), 151.3, 139.7, 135.4 (d, J = 3.5 Hz), 134.7, 130.5 (d, J = 8.1 Hz), 130.1, 123.0, 120.8, 115.5 (d, J = 21.6 Hz), 51.5, 28.2, 21.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ –113.9 (m); IR (cm^{-1}) 3307, 2969, 1764, 1636, 1604, 1543, 1513, 1476, 1369, 1205, 1173, 857; HRMS (EI) m/z calcd. for $C_{19}H_{20}FNO_3$ $[M]^+$: 329.1427, found: 329.1428.



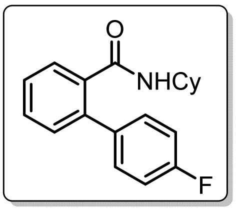
***N*-(*tert*-Butyl)-3-(4-fluorophenyl)-2-naphthamide** (Table 3, **3o**)

White solid; m.p. 185-186 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.55 – 7.50 (m, 2H), 7.47 (dd, J = 8.4, 5.5 Hz, 2H), 7.14 (dd, J = 8.6, 8.6 Hz, 2H), 5.21 (s, 1H), 1.21 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 162.5 (d, J = 247.9 Hz), 136.5 (d, J = 3.3 Hz), 135.7, 135.1, 133.5, 132.0, 130.7 (d, J = 8.3 Hz), 129.2, 128.7, 128.2, 127.7, 127.5, 126.8, 115.4 (d, J = 24.0 Hz), 51.6, 28.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.7 (m); IR (cm^{-1}) 3277, 2987, 1634, 1547, 1511, 1389, 1360, 1334, 1309, 1220, 1161, 836; HRMS (EI) m/z calcd. for $C_{21}H_{20}FNO$ $[M]^+$: 321.1529, found: 321.1528.



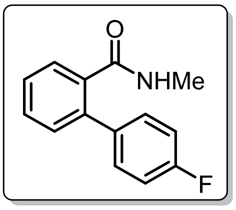
N-Adamantanyl-4'-fluoro-[1,1'-biphenyl]-2-carboxamide (Table 3, **3p**)

White solid; m.p. 150-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.30 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.13 (dd, *J* = 8.6, 8.6 Hz, 2H), 4.94 (s, 1H), 2.00 (s, 3H), 1.78 (d, *J* = 3.0 Hz, 6H), 1.64 – 1.59 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 162.5 (d, *J* = 249.1 Hz), 138.1, 137.1, 136.4 (d, *J* = 3.5 Hz), 130.5 (d, *J* = 7.5 Hz), 130.0, 129.7, 128.6, 127.6, 115.4 (d, *J* = 21.3 Hz), 52.2, 41.1, 36.2, 29.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.8 (m); IR (cm^{-1}) 3296, 2905, 2847, 1633, 1557, 1512, 1330, 1247, 1155, 1090, 832, 760; HRMS (EI) m/z calcd. for $C_{23}H_{24}FNO$ $[M]^+$: 349.1842, found: 349.1844.



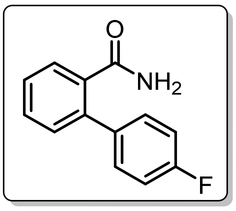
N-Cyclohexyl-4'-fluoro-[1,1'-biphenyl]-2-carboxamide (Table 3, **3q**)

White solid; m.p. 174-175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.41 – 7.38 (m, 3H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.10 (dd, *J* = 8.6, 8.6 Hz, 2H), 5.13 (d, *J* = 8.5 Hz, 1H), 3.79 – 3.73 (m, 1H), 1.68 – 1.65 (m, 2H), 1.55 – 1.50 (m, 3H), 1.31 – 1.25 (m, 2H), 1.08 – 1.01 (m, 1H), 0.83 – 0.77 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 162.5 (d, *J* = 246.8 Hz), 138.2, 136.3, 136.3, 130.3 (d, *J* = 8.9 Hz), 130.0, 129.9, 128.6, 127.6, 115.4 (d, *J* = 21.7 Hz), 48.2, 32.5, 25.3, 24.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.6 (m); IR (cm^{-1}) 3251, 2929, 2855, 1629, 1556, 1514, 1334, 1223, 1081, 1007, 838, 762; HRMS (EI) m/z calcd. for $C_{19}H_{20}FNO$ $[M]^+$: 297.1529, found: 297.1527.



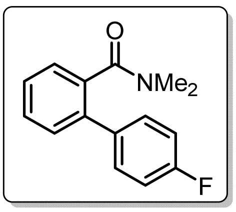
N-Methyl-4'-fluoro-[1,1'-biphenyl]-2-carboxamide (Table 3, **3r**)

White solid; m.p. 127-128 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.34 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.10 (dd, *J* = 8.6, 8.6 Hz, 2H), 5.31 (s, 1H), 2.71 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 162.5 (d, *J* = 246.7 Hz), 138.3, 136.2 (d, *J* = 3.5 Hz), 135.9, 130.2 (d, *J* = 8.2 Hz), 130.1, 128.6, 127.7, 115.6 (d, *J* = 22.1 Hz), 26.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.6 (m); IR (cm^{-1}) 3254, 2924, 1632, 1549, 1510, 1439, 1403, 1325, 1217, 1156, 837, 766; HRMS (ESI) m/z calcd. for $C_{14}H_{12}FNO$ $[M+Na]^+$: 252.0795, found: 252.0785.



4'-Fluoro-[1,1'-biphenyl]-2-carboxamide (Table 3, **3s**)

White solid; m.p. 148-149 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.11 (dd, *J* = 8.4, 8.4 Hz, 2H), 5.75 (s, 1H), 5.31 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 162.6 (d, *J* = 245.3 Hz), 138.7, 136.1 (d, *J* = 3.3 Hz), 134.6, 130.5, 130.4, 130.4, 128.8, 127.7, 115.6 (d, *J* = 22.3 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.3 (m); IR (cm^{-1}) 3887, 3166, 2922, 1698, 1645, 1614, 1509, 1480, 1394, 1218, 1113, 1016; HRMS (ESI) m/z calcd. for $C_{13}H_{10}FNO$ $[M+Na]^+$: 238.0639, found: 238.0648.

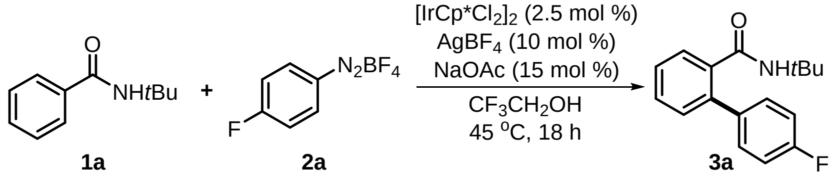


4'-Fluoro-N,N-dimethyl-[1,1'-biphenyl]-2-carboxamide (Table 3, **3t**)

Colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 3H), 7.39 – 7.36 (m, 3H), 7.08 (dd, *J*

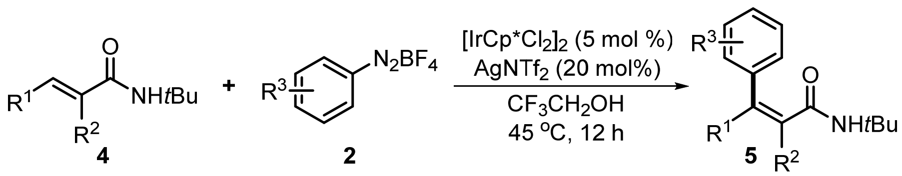
= 8.4, 8.4 Hz, 2H), 2.85 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 162.5 (d, *J* = 249.3 Hz), 137.6, 136.0 (d, *J* = 3.4 Hz), 135.8, 130.2 (d, *J* = 7.7 Hz), 129.3, 129.3, 127.8, 127.3, 115.3 (d, *J* = 21.4 Hz), 37.9, 34.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ –114.8 (m); IR (cm^{-1}) 3061, 2926, 1626, 1604, 1513, 1475, 1393, 1222, 1161, 1097, 1044, 1007; HRMS (ESI) m/z calcd. for $C_{15}H_{14}FNO$ $[M+Na]^+$: 266.0952, found: 266.0956.

2. Procedure for the Ir-Catalyzed C–H Arylation Reaction of Benzamide 1a with Aryldiazonium Tetrafluoroborate 2a on Gram Scale (Eq. 1)

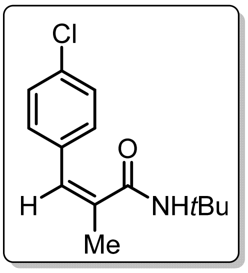


To an oven-dried round-bottomed flask equipped with a Teflon stirbar were added *N-tert*-butylbenzamide (**1a**, 1329.4 mg, 7.5 mmol), 4-fluorophenyldiazonium tetrafluoroborate (**2a**, 1049.6 mg, 5.0 mmol), $[IrCp^*Cl_2]_2$ (99.6 mg, 0.125 mmol, 2.5 mol %), $AgBF_4$ (97.3 mg, 0.5 mmol, 10 mol %), NaOAc (61.5 mg, 0.75 mmol, 15 mol %) and 2,2,2-trifluoroethanol (25 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 45 °C for 18 h, filtered through a pad of celite with CH_2Cl_2 (10 mL x 4) and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography with *n*-pentane/EtOAc as an eluent to give the desired arylated product **3a** (986.5 mg, 73%).

3. Procedure for the Ir-Catalyzed C–H Arylation Reaction of Enamides with Aryldiazonium Tetrafluoroborates (Table 4)

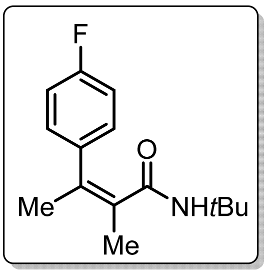


To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added enamide (**4**, 0.3 mmol), aryldiazonium tetrafluoroborate (**2**, 0.2 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.01 mmol, 5 mol %), $AgNTf_2$ (15.5 mg, 0.04 mmol, 20 mol %) and 2,2,2-trifluoroethanol (1.0 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 45 °C for 12 h, filtered through a pad of silica with *n*-hexane/EtOAc (2:1, 10 mL x 4) and concentrated under reduced pressure. The crude reaction mixture was further purified by silica gel column chromatography with *n*-hexane/EtOAc as an eluent to give the desired arylated product **5**.



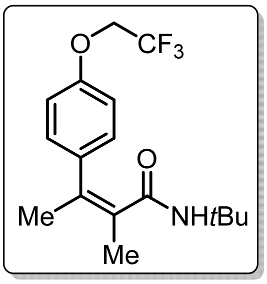
***(Z)-N-*(*tert*-Butyl)-3-(4-chlorophenyl)-2-methylacrylamide** (Table 4, **5a**)

Beige solid; m.p. 163-164 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.36 (s, 1H), 5.11 (s, 1H), 2.05 (d, *J* = 1.6 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 137.3, 134.5, 133.3, 129.6, 128.4, 126.8, 51.2, 28.3, 21.9; IR (cm^{-1}) 3276, 2965, 2914, 1622, 1552, 1487, 1359, 1267, 1225, 1086, 1011, 875; HRMS (EI) m/z calcd. for $C_{14}H_{18}ClNO$ $[M]^+$: 251.1077, found: 251.1077.



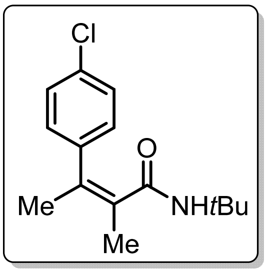
***(Z)-N-*(*tert*-Butyl)-3-(4-fluorophenyl)-2-methylbut-2-enamide** (Table 4, **5b**)

White solid; m.p. 122-123 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 (dd, *J* = 8.7, 8.7 Hz, 2H), 4.72 (s, 1H), 2.01 (s, 3H), 1.97 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 161.9 (d, *J* = 246.6 Hz), 139.2 (d, *J* = 3.6 Hz), 134.4, 132.6, 129.2 (d, *J* = 8.4 Hz), 115.2 (d, *J* = 21.4 Hz), 50.7, 28.1, 20.7, 16.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ –115.1 (m); IR (cm^{-1}) 3288, 2972, 1625, 1604, 1530, 1507, 1480, 1450, 1365, 1219, 1154, 836; HRMS (EI) m/z calcd. for $C_{15}H_{20}FNO$ $[M]^+$: 249.1529, found: 249.1531.



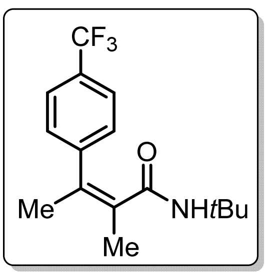
***(Z)*-*N*-(*tert*-Butyl)-2-methyl-3-[4-(2,2,2-trifluoroethoxy)phenyl]but-2-enamide** (Table 4, **5b'**)

White solid; m.p. 100-101 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.73 (s, 1H), 4.35 (q, *J* = 8.1 Hz, 2H), 2.01 (s, 3H), 1.97 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 156.6, 137.6, 134.7, 132.3, 129.0, 123.3 (q, *J* = 279.3 Hz), 114.9, 66.0 (q, *J* = 36.0 Hz), 50.7, 28.2, 20.7, 16.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ –74.0 (t, *J* = 8.1 Hz); IR (cm^{-1}) 3441, 2962, 2922, 2853, 1654, 1505, 1452, 1298, 1229, 1077, 967, 863; HRMS (EI) m/z calcd. for $C_{17}H_{22}F_3NO_2$ $[M]^+$: 329.1603, found: 329.1602.



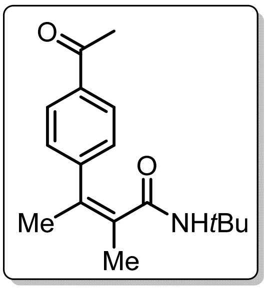
***(Z)*-*N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methylbut-2-enamide** (Table 4, **5c**)

White solid; m.p. 162-163 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.73 (s, 1H), 2.01 (s, 3H), 1.98 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 141.6, 134.2, 132.9, 132.9, 129.0, 128.5, 50.7, 28.1, 20.5, 16.7; IR (cm^{-1}) 3304, 2974, 2914, 1626, 1527, 1491, 1391, 1378, 1222, 1087, 1014, 829; HRMS (EI) m/z calcd. for $C_{15}H_{20}ClNO$ $[M]^+$: 265.1233, found: 265.1232.



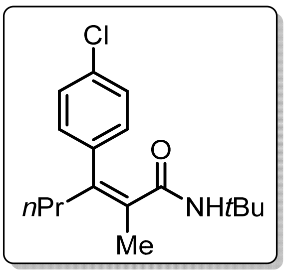
***(Z)*-*N*-(*tert*-Butyl)-2-methyl-3-[4-(trifluoromethyl)phenyl]but-2-enamide** (Table 4, **5d**)

White solid; m.p. 117-118 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 1H), 2.04 (s, 3H), 2.00 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 147.0, 134.0, 133.7, 129.3 (q, *J* = 32.8 Hz), 128.0, 125.3 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 272.1 Hz), 50.8, 28.0, 20.2, 16.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.6 (s); IR (cm^{-1}) 3304, 2967, 1625, 1524, 1324, 1223, 1192, 1153, 1119, 1071, 1016, 844; HRMS (EI) m/z calcd. for $C_{16}H_{20}F_3NO$ $[M]^+$: 299.1497, found: 299.1496.



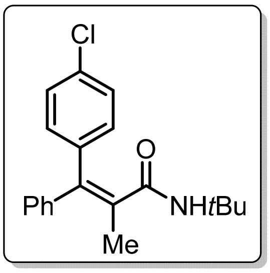
***(Z)*-*N*-(*tert*-Butyl)-3-(4-acetylphenyl)-2-methylbut-2-enamide** (Table 4, **5e**)

White solid; m.p. 116-117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.74 (s, 1H), 2.60 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 170.3, 148.2, 135.8, 134.4, 133.5, 128.4, 127.9, 50.8, 28.1, 26.6, 20.2, 16.8; IR (cm^{-1}) 3264, 2965, 2920, 1678, 1644, 1625, 1537, 1378, 1268, 1224, 956, 838; HRMS (EI) m/z calcd. for $C_{17}H_{23}NO_2$ $[M]^+$: 273.1729, found: 273.1730.



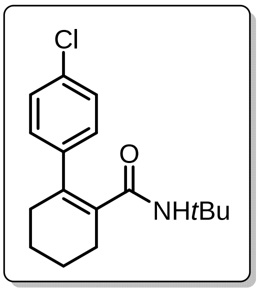
***(Z)*-*N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methylhex-2-enamide** (Table 4, **5f**)

White solid; m.p. 115-116 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.99 (s, 3H), 1.32 – 1.26 (m, 2H), 0.99 (s, 9H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 140.6, 138.9, 133.1, 132.9, 129.4, 128.5, 50.7, 36.0, 28.1, 20.6, 16.2, 13.8; IR (cm^{-1}) 3300, 2956, 2924, 1623, 1528, 1488, 1447, 1392, 1224, 1092, 1014, 829; HRMS (EI) m/z calcd. for $C_{17}H_{24}ClNO$ $[M]^+$: 293.1546, found: 293.1544.



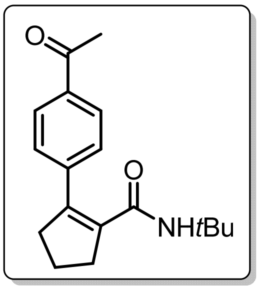
***(Z)*-*N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methyl-3-phenylacrylamide** (Table 4, **5g**)

White solid; m.p. 139-140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 2H), 4.97 (s, 1H), 1.99 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 140.5, 140.1, 139.6, 135.0, 133.4, 130.6, 129.5, 128.4, 128.2, 127.5, 51.1, 28.2, 18.7; IR (cm^{-1}) 3324, 2971, 1631, 1535, 1491, 1451, 1361, 1303, 1290, 1092, 1017, 827; HRMS (EI) m/z calcd. for $C_{20}H_{22}ClNO$ $[M]^+$: 327.1390, found: 327.1389.



***N*-(*tert*-Butyl)-2-(4-chlorophenyl)cyclohex-1-ene-1-carboxamide** (Table 4, **5h**)

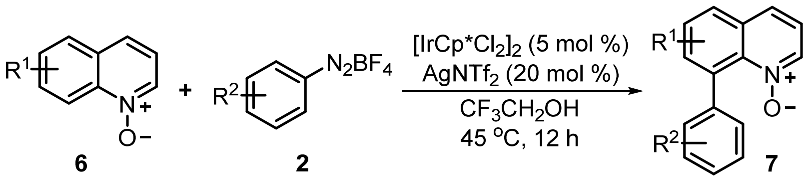
White solid; m.p. 111-112 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.75 (s, 1H), 2.41 – 2.38 (m, 2H), 2.31 – 2.29 (m, 2H), 1.75 – 1.68 (m, 4H), 1.03 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 140.9, 136.4, 135.0, 133.1, 128.9, 128.5, 50.7, 31.2, 28.1, 26.8, 22.6, 21.9; IR (cm^{-1}) 3317, 3254, 2924, 1623, 1543, 1489, 1360, 1306, 1222, 1091, 1015, 826; HRMS (EI) m/z calcd. for $C_{17}H_{22}ClNO$ $[M]^+$: 291.1390, found: 291.1389.



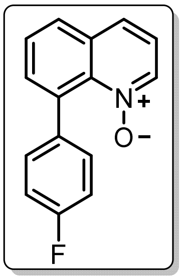
***N*-(*tert*-Butyl)-2-(4-acetylphenyl)cyclopent-1-ene-1-carboxamide** (Table 4, **5i**)

White solid; m.p. 134-135 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.11 (s, 1H), 2.83 (t, *J* = 7.6 Hz, 4H), 2.61 (s, 3H), 2.01 (p, *J* = 7.6 Hz, 2H), 1.21 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.4, 166.7, 141.7, 141.4, 137.6, 136.2, 128.3, 127.9, 51.1, 38.3, 36.1, 28.4, 26.6, 22.0; IR (cm^{-1}) 3256, 2961, 2922, 1677, 1616, 1543, 1448, 1358, 1276, 1223, 958, 835; HRMS (EI) m/z calcd. for $C_{18}H_{23}NO_2$ [*M*]$^+$: 285.1729, found: 285.1725.

4. Procedure for the Ir-Catalyzed C–H Arylation Reaction of Quinoline *N*-Oxides with Aryldiazonium Tetrafluoroborates (Table 5)

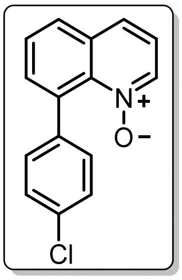


To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added quinoline *N*-oxide (**6**, 0.2 mmol), aryldiazonium tetrafluoroborate (**2**, 0.3 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.01 mmol, 5 mol %), $AgNTf_2$ (15.5 mg, 0.04 mmol, 20 mol %) and 2,2,2-trifluoroethanol (1.0 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 45 °C for 12 h, filtered through a pad of silica with CH_2Cl_2/acetone (5:1, 10 mL x 4) and concentrated under reduced pressure. The crude reaction mixture was further purified by silica gel column chromatography with toluene/EtOAc as an eluent to give the desired arylated product **7**.



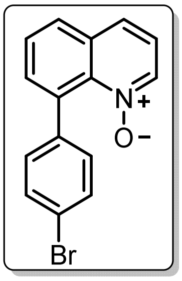
8-(4-Fluorophenyl)quinoline 1-oxide (Table 5, **7a**)

Beige solid; m.p. 137-138 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 6.0, 1.2 Hz, 1H), 7.89 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.76 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.51 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.06 (dd, *J* = 8.7, 8.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, *J* = 244.1 Hz), 139.2, 138.5 (d, *J* = 3.5 Hz), 137.0, 135.4, 134.3, 132.1, 129.5 (d, *J* = 8.2 Hz), 128.6, 127.6, 125.9, 121.3, 113.7 (d, *J* = 21.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –117.1 (m); IR (cm^{-1}) 2924, 2854, 1510, 1500, 1303, 1289, 1234, 1206, 1160, 1079, 845, 816; HRMS (EI) m/z calcd. for $C_{15}H_{10}FNO$ [*M*]$^+$: 239.0746, found: 239.0743. [Note: trace (<4%) amount of ipso-substitued side product is incorporated]



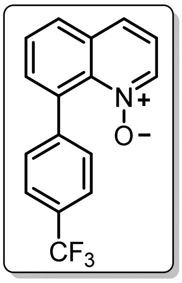
8-(4-Chlorophenyl)quinoline 1-oxide (Table 5, **7b**)

Beige solid; m.p. 166-167 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.0 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.49 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 8.4, 6.1 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.1, 139.0, 136.9, 135.1, 134.1, 132.1, 132.0, 129.3, 128.7, 127.6, 126.9, 125.9, 121.3; IR (cm^{-1}) 3068, 2922, 1562, 1487, 1413, 1379, 1304, 1241, 1231, 1079, 934, 821; HRMS (EI) m/z calcd. for $C_{15}H_{10}ClNO$ [*M*]$^+$: 255.0451, found: 255.0450.



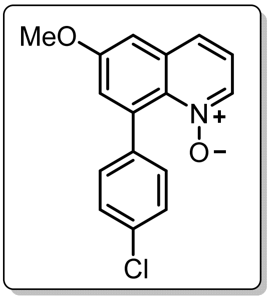
8-(4-Bromophenyl)quinoline 1-oxide (Table 5, **7c**)

Beige solid; m.p. 176-177 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 6.1, 1.2 Hz, 1H), 7.89 (d, *J* = 0.9 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.49 – 7.48 (m, 3H), 7.29 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.6, 139.0, 136.9, 135.1, 134.0, 132.0, 129.9, 129.7, 128.8, 127.6, 125.9, 121.3, 120.3; IR (cm^{-1}) 3069, 2923, 1562, 1486, 1414, 1380, 1306, 1231, 1173, 1009, 933, 820; HRMS (EI) m/z calcd. for $C_{15}H_{10}BrNO$ [*M*]$^{+}$: 298.9946, found: 298.9944.



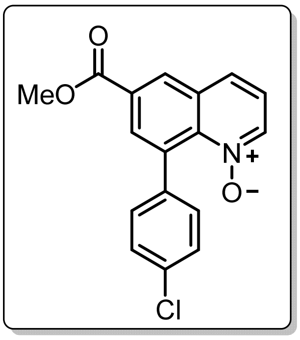
8-[4-(Trifluoromethyl)]quinoline 1-oxide (Table 5, **7d**)

White solid; m.p. 202-203 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.0 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.62 (dd, *J* = 15.2, 7.7 Hz, 3H), 7.50 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.32 (dd, *J* = 8.4, 6.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 138.9, 136.8, 135.0, 134.0, 132.0, 129.0, 128.3 (q, *J* = 31.5 Hz), 128.2, 127.7, 126.0, 124.5 (q, *J* = 270.6 Hz), 123.8 (q, *J* = 3.9 Hz), 121.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.3 (s); IR (cm^{-1}) 3079, 2925, 1570, 1419, 1404, 1243, 1150, 1104, 1062, 1017, 836, 752; HRMS (EI) m/z calcd. for $C_{16}H_{10}F_3NO$ [*M*]$^{+}$: 289.0714, found: 289.0711.



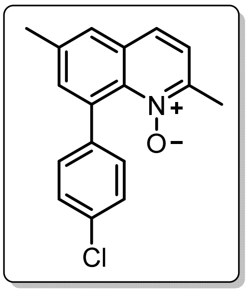
8-(4-Chlorophenyl)-6-methoxyquinoline 1-oxide (Table 5, **7e**)

Grey solid; m.p. 180-181 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.13 (d, *J* = 5.6 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 140.7, 136.8, 135.0, 134.9, 133.5, 132.2, 129.2, 126.9, 126.0, 125.0, 121.7, 106.4, 55.7; IR (cm^{-1}) 2922, 2849, 1603, 1514, 1490, 1325, 1232, 1172, 1087, 975, 901, 828; HRMS (EI) m/z calcd. for $C_{16}H_{12}ClNO_2$ $[M]^+$: 285.0557, found: 285.0555.



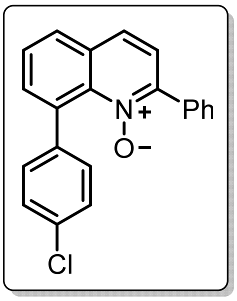
8-(4-Chlorophenyl)-6-methoxycarbonylquinoline 1-oxide (Table 5, **7f**)

Light yellow solid; m.p. 224-225 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.9 Hz, 1H), 8.41 (dd, *J* = 6.1, 1.2 Hz, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.26 (d, *J* = 8.3 Hz, 2H), 3.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 140.7, 140.3, 138.5, 135.8, 133.3, 132.6, 131.7, 131.2, 129.3, 129.2, 127.1, 126.6, 122.2, 52.7; IR (cm^{-1}) 3051, 2949, 1720, 1488, 1440, 1377, 1238, 1118, 1084, 997, 821, 805; HRMS (EI) m/z calcd. for $C_{17}H_{12}ClNO_3$ $[M]^+$: 313.0506, found: 313.0507.



8-(4-Chlorophenyl)-2,6-dimethylquinoline 1-oxide (Table 5, **7g**)

Beige solid; m.p. 160-161 °C; ^{1}H NMR (400 MHz, methanol-d_4) δ 7.91 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 0.9 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 2.53 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, methanol-d_4) δ 148.8, 143.5, 139.0, 138.5, 138.3, 135.4, 133.0, 132.6, 131.1, 129.6, 129.3, 127.9, 124.8, 21.1, 19.0; IR (cm^{-1}) 3024, 2919, 1568, 1488, 1323, 1248, 1227, 1135, 1100, 1084, 1057, 864; HRMS (EI) m/z calcd. for $C_{17}H_{14}ClNO$ $[M]^+$: 283.0764, found: 283.0761.



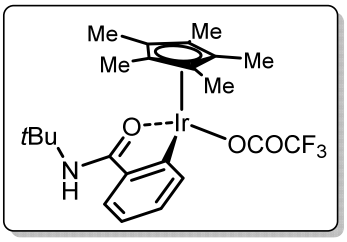
8-(4-Chlorophenyl)-2-phenylquinoline 1-oxide (Table 5, **7h**)

Light yellow solid; m.p. 231-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.58 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.47 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.43 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.38 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.8, 142.0, 139.8, 135.6, 134.7, 133.7, 131.8, 131.2, 129.4, 129.2, 129.2, 128.6, 128.3, 127.3, 127.0, 124.8, 123.8; IR (cm^{-1}) 3046, 2953, 1559, 1487, 1446, 1341, 1305, 1220, 1080, 1012, 936, 757; HRMS (EI) m/z calcd. for $C_{21}H_{14}ClNO$ $[M]^+$: 331.0764, found: 331.0766.

V. Procedures for Mechanistic Studies

1. Preparation of *BA-Iridacycle*[S5]

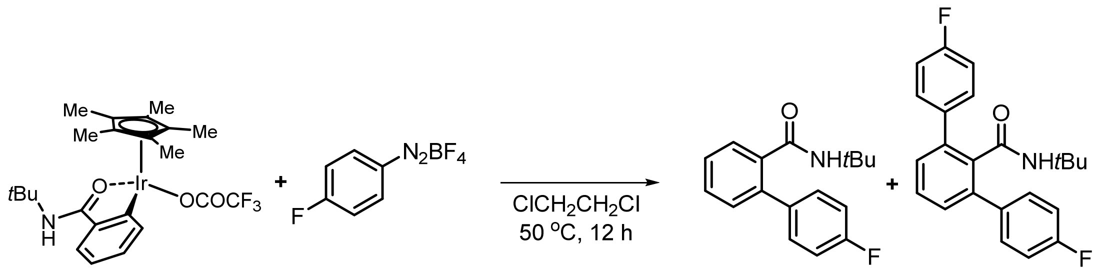
A solution of *N*-*tert*-butylbenzamide (0.89 g, 5.0 mmol), $[IrCp^*Cl_2]_2$ (1.99 g, 2.5 mmol), lithium carbonate (0.37 g, 5.0 mmol), and silver trifluoroacetate (1.10 g, 5.0 mmol) in 1,2-dichloroethane (100 mL) was stirred for 12 h at room temperature under argon atmosphere. Another portion of silver trifluoroacetate (1.10 g, 5.0 mmol) was added and the mixture was allowed to stir for additional 12 h at room temperature. The resulting crude mixture was filtered through a pad of celite washing with 1,2-dichloroethane (50 mL), and concentrated under reduced pressure. EtOAc (10 mL) was added to the crude product, and the resulting yellow precipitate was collected by careful filtration and washed with EtOAc (10 mL). The precipitate was dried under reduced pressure to give the desired iridacycle as a yellow solid (1.33 g, 43%)



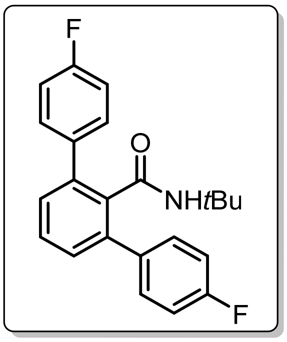
BA-Iridacycle (Scheme 2)

Yellow solid; m.p. 223–224 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.25 (d, *J* = 6.1 Hz, 1H), 7.09 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.96 (dd, *J* = 7.0, 7.0 Hz, 1H), 6.22 (s, 1H), 1.71 (s, 15H), 1.48 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.2, 168.3, 162.2 (q, *J* = 35.4 Hz), 140.4, 136.7, 132.5, 124.2, 122.2, 115.5 (q, *J* = 292.9 Hz), 85.5, 53.0, 29.1, 9.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ –74.7 (s); IR (cm^{-1}) 3331, 2969, 2922, 1687, 1594, 1567, 1532, 1411, 1346, 1194, 1134, 741; HRMS (EI) m/z calcd. for $C_{23}H_{29}F_3IrNO_3$ $[M]^+$: 617.1729, found: 617.1726.

2. Stoichiometric Arylation of *BA-Iridacycle* with Aryldiazonium Salt 2a (Scheme 2)



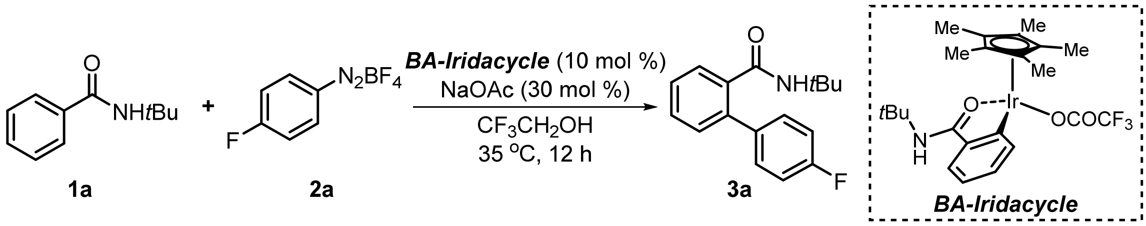
To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added ***BA-Iridacycle*** (61.7 mg, 0.1 mmol), 4-fluorophenyldiazonium tetrafluoroborate (**2a**, 23.1 mg, 0.11 mmol) and 2,2,2-trifluoroethanol (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 50 ^{o}C for 12 h, filtered through a pad of silica with *n*-hexane/EtOAc (2:1, 10 mL x 4) and concentrated under reduced pressure. The crude mixture was further purified by silica gel column chromatography with *n*-hexane/EtOAc as an eluent to give the desired mono-arylated product **3a** (26%) and bis-arylated product **3a’** (28%).



***N*-(*tert*-Butyl)-4,4''-difluoro-[1,1':3',1''-terphenyl]-2'-carboxamide** (Scheme 2, **3a’**)

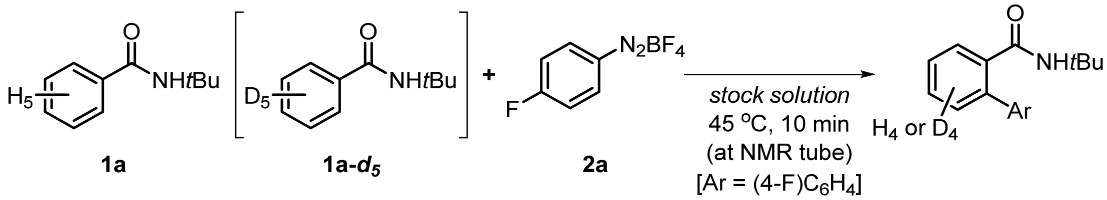
White solid; m.p. 261-262 ^{o}C; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 – 7.43 (m, 5H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.08 (dd, *J* = 8.6, 8.6 Hz, 4H), 5.02 (s, 1H), 0.97 (s, 9H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 167.5, 162.4 (d, *J* = 246.4 Hz), 138.9, 137.0, 136.3 (d, *J* = 3.7 Hz), 130.6 (d, *J* = 8.2 Hz), 129.1, 128.7, 115.0 (d, *J* = 21.6 Hz), 51.5, 28.1; ^{19}F NMR (564 MHz, CDCl$_3$) δ –115.2 (m); IR (cm^{-1}) 3296, 2959, 1632, 1604, 1544, 1508, 1454, 1316, 1217, 1160, 840, 808; HRMS (EI) m/z calcd. for $C_{23}H_{21}F_2NO$ $[M]^+$: 365.1591, found: 365.1592.

3. Catalytic C−H Arylation Reaction using *BA-Iridacycle* (Scheme 5a)



To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *N*-*tert*-butylbenzamide (**1a**, 26.6 mg, 0.15 mmol), 4-fluorophenyldiazonium tetrafluoroborate (**2a**, 21.0 mg, 0.1 mmol), ***BA-Iridacycle*** (6.2 mg, 0.01 mmol, 10 mol %), NaOAc (2.5 mg, 0.03 mmol, 30 mol %) and 2,2,2-trifluoroethnanol (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 35 °C for 12 h. The reaction mixture was filtered through a pad of silica with *n*-hexane/EtOAc (2:1, 10 mL x 4) and concentrated under reduced pressure. The crude yield of **3a** (60%) was measured by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard.

4. Deuterium Kinetic Isotope Effect: Initial Rate Comparison Test (Scheme 5b)



- Preparation of '*stock solution*': To a 5 mL glass vial were added $[IrCp^*Cl_2]_2$ (6.0 mg, 0.0075 mmol), $AgBF_4$ (5.8 mg, 0.03 mmol), NaOAc (3.7 mg, 0.045 mmol) and 2,2,2-trifluoroethanol-*d*$_3$ (1.5 mL) under argon atmosphere. The mixture was shaken over 3 min to insure complete mixing of the reagents. Resulting precipitate was removed by filtering through a syringe filter (PTFE, 0.5 µm) and the clear yellow filtrate was used as '*stock solution*'.

- Experimental Procedure: To a J-Young NMR tube were added 4-fluorophenyldiazonium tetrafluoroborate (**2a**, 10.5 mg, 0.05 mmol), 1,1,2,2-tetrachloroethane as an internal standard (5.3 µL, 0.05 mmol) and stock solution (0.5 mL, 0.1 M) under atmospheric conditions. The NMR tube was gently shaken and pre-heated at 45 °C over 15 min. *N*-*tert*-butylbenzamide (**1a**, 13.3 mg, 0.075 mmol) or *N*-*tert*-butyl-*d*$_5$-benzamide (**1a-*d*$_5$**, 13.7 mg, 0.075 mmol) was added, and the NMR tube was again shaken to insure thorough mixing of the reagents and started to measure its conversion over 10 min with a 1 min interval at the 45 °C (NMR probe temperature). KIE value (k_H/k_D = 1.20) was determined by comparing the relative initial rates.

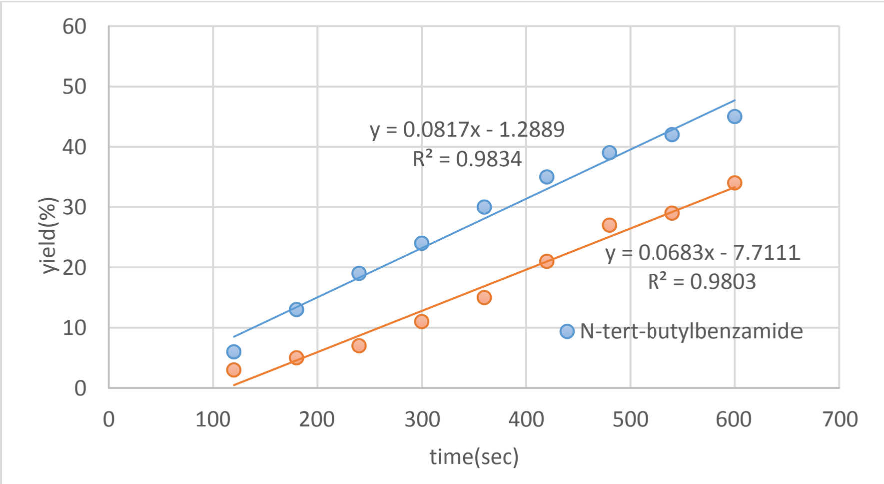
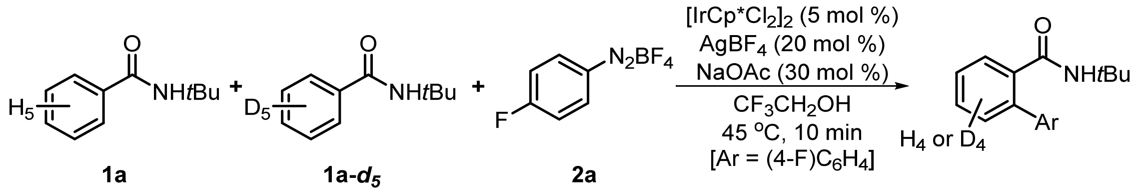


Figure S1. Initial rate of *N-tert*-butylbenzamide (**1a**, blue dot) and *N-tert*-butylbenzamide-d_5 (**1a-d_5**, red dot)

5. Deuterium Kinetic Isotope Effect: Intermolecular Competition Test (Scheme 5b)



To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added 4-fluorophenyldiazonium tetrafluoroborate (**2a**, 42.0 mg, 0.2 mmol), $[IrCp^*Cl_2]_2$ (8.0 mg, 0.01 mmol, 5 mol %), $AgBF_4$ (7.8 mg, 0.04 mmol, 20 mol %), NaOAc (4.9 mg, 0.06 mmol, 30 mol %) and 2,2,2-trifluoroethanol (1.0 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 45 °C for 20 min and then *N-tert*-butylbenzamide (**1a**, 26.6 mg, 0.15 mmol) and *N-tert*-butyl-d_5-benzamide (**1a-*d*$_5$**, 27.4 mg, 0.15 mmol) were added. The mixture was further stirred in a oil bath at 45 °C for 10 min and filtered through a pad of silica washing with *n*-hexane/EtOAc (2:1, 10 mL x 4). Organic solvents were removed under reduced pressure and the crude mixture was further purified by silica gel column chromatography with *n*-hexane/EtOAc as an eluent to recover the starting material and the desired arylated product. KIE value (P_H/P_D = 1.65) was determined by the ratio of desired product.

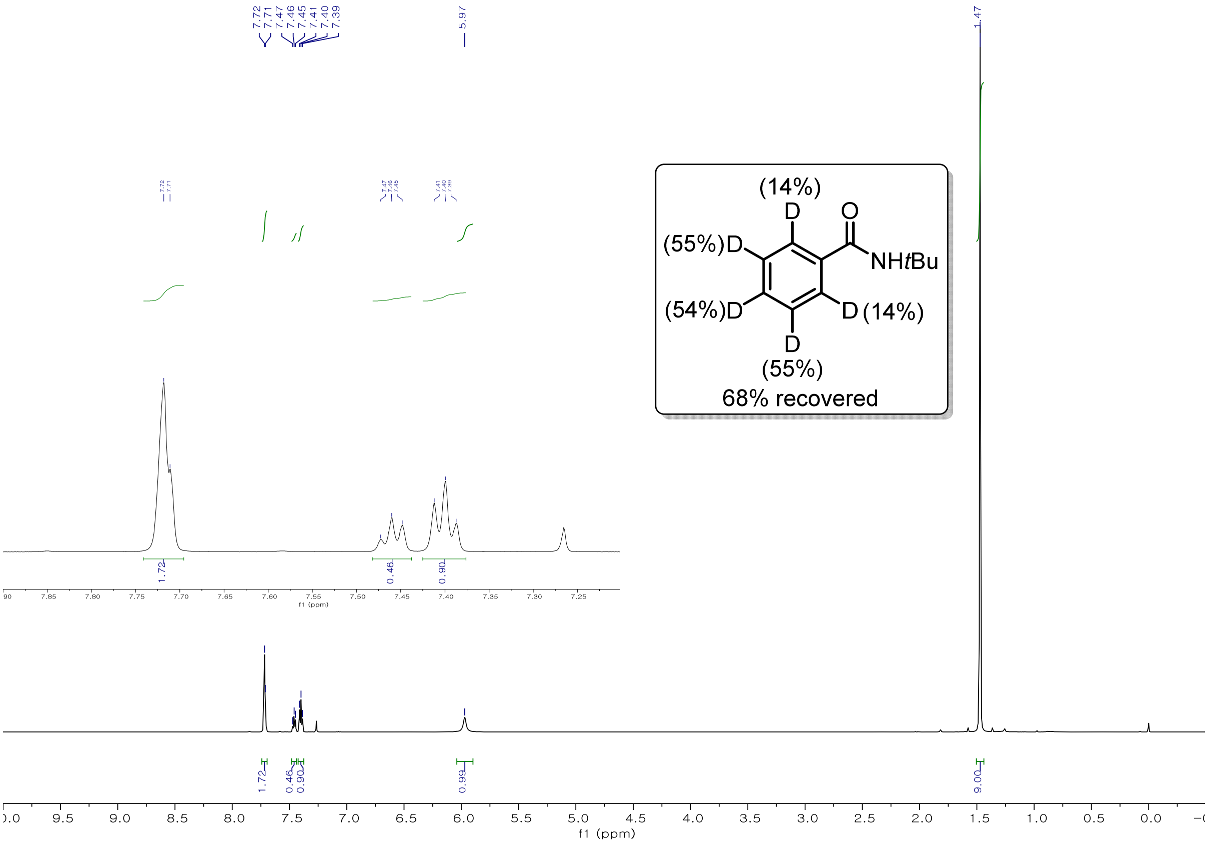


Figure S2. ^{1}H NMR of intermolecular competition test: recovered starting material

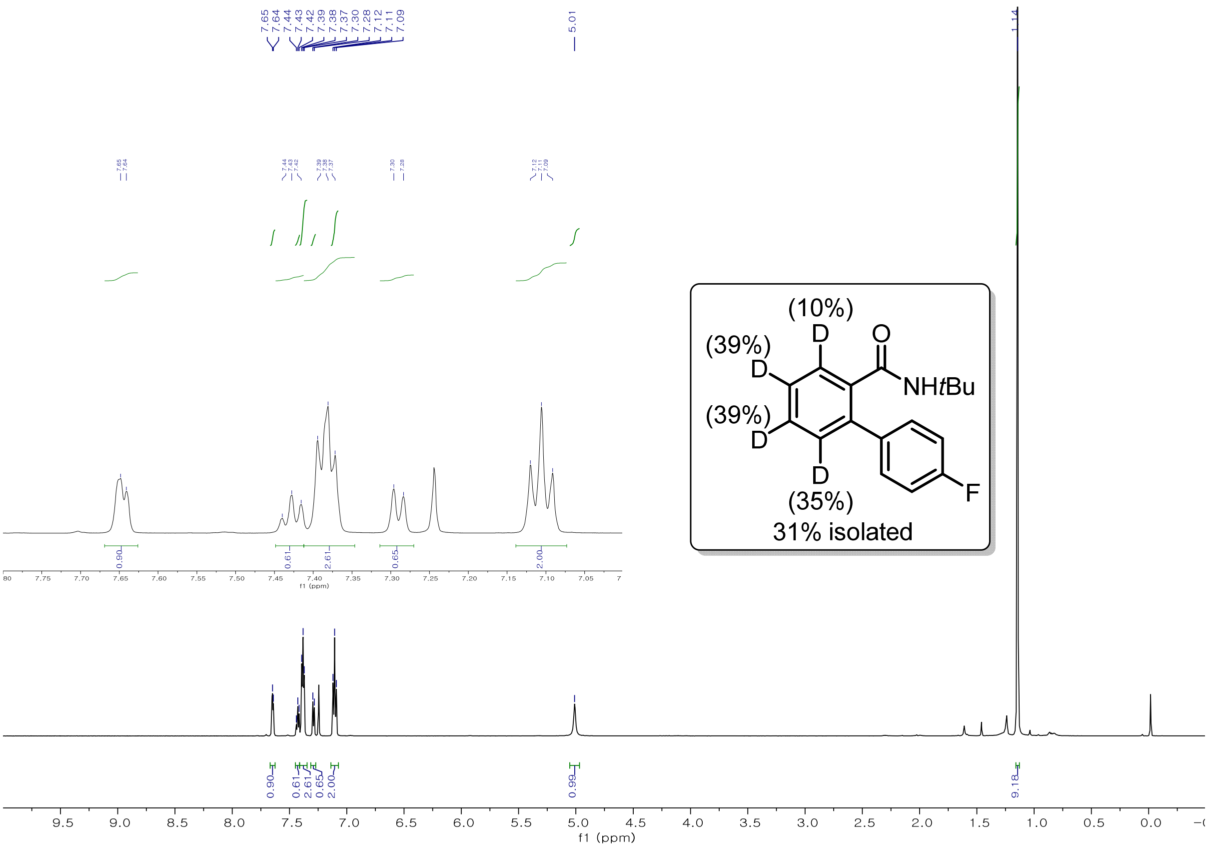
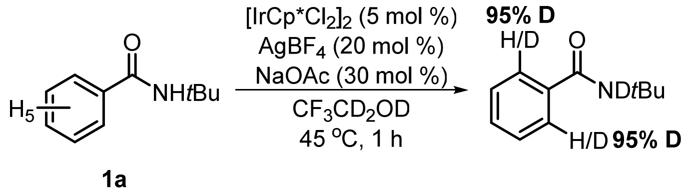


Figure S3. ^{1}H NMR of intermolecular competition test: arylated product

6. Deuterium Kinetic Isotope Effect: H/D Scrambling Test (Scheme 5c)



To an oven-dried screw capped vial equipped with a spinvane triangular-shaped Teflon stirbar were added *N*-*tert*-butylbenzamide (**1a**, 17.7 mg, 0.1 mmol), $[IrCp^*Cl_2]_2$ (4.0 mg, 0.005 mmol, 5 mol %), $AgBF_4$ (3.9 mg, 0.02 mmol, 20 mol %), NaOAc (2.5 mg, 0.03 mmol, 30 mol %) and 2,2,2-trifluoroethanol-d_3 (0.5 mL) under argon atmosphere. The reaction mixture was stirred in a pre-heated oil bath at 45 °C for 1 h and filtered through a pad of silica washing with *n*-hexane/EtOAc (2:1, 10 mL x 4). Organic solvents were removed under reduced pressure and the deuterium incorporation was determined by ^{1}H NMR spectroscopy of the crude mixture.

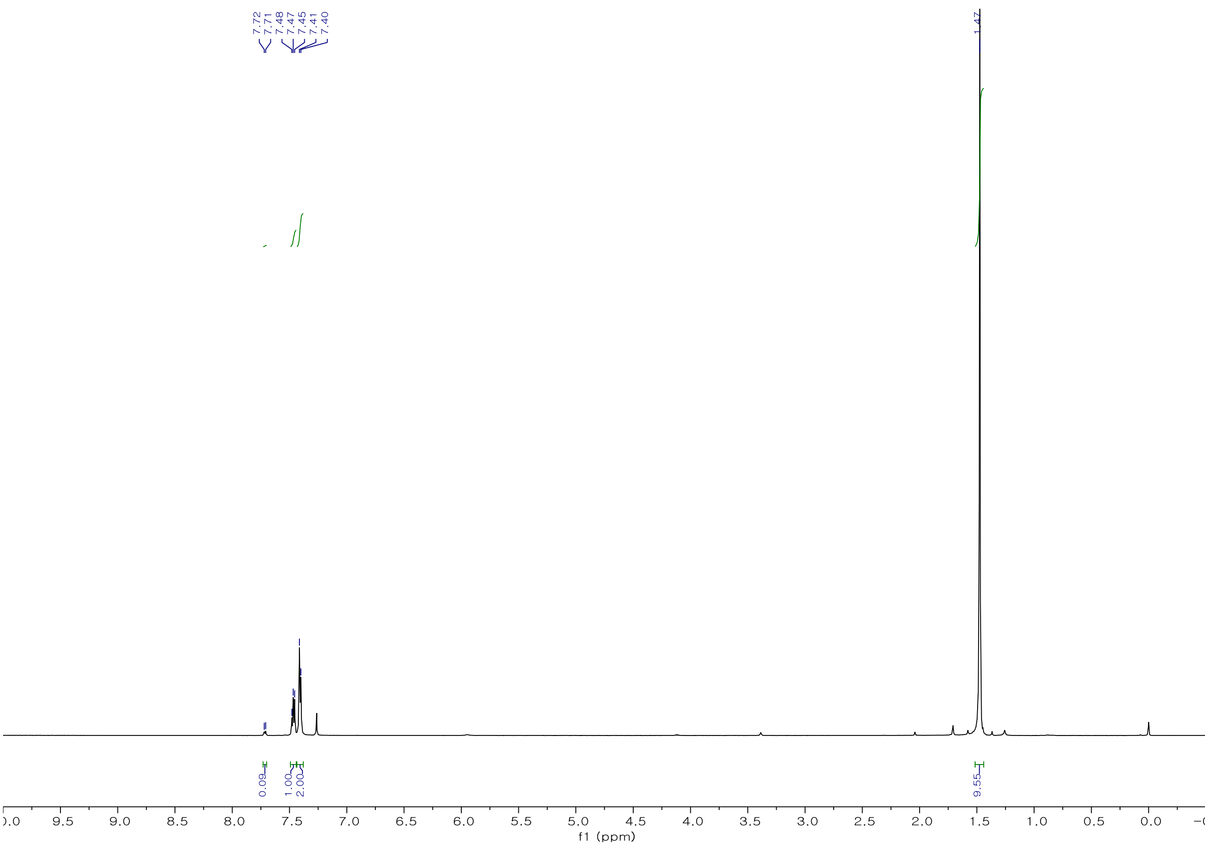


Figure S4. ^{1}H NMR of H/D scrambling test

VI. Computational Studies and Coordinates of Optimized Structures and Transition States

1. Computational Details

DFT calculations was carried out by using M06 method.[S6] To optimize geometry structure and vibrational frequencies, Los Alamos National Laboratory 2 ζ (LANL2DZ) ECP basis set [S7] was used for iridium atom, while using the 6-31G* basis set for all other atoms. Subsequent single point energies were calculated with LANL2DZ ECP and 6-311+G** basis set. Energetics calculated under standard conditions (1 atm. and 298.15 K) and reported as free energies in kcal/mol. Solvent effects were accounted at the PCM method [S8] in 2,2,2-trifluoroethanol (ε= 26.726) as the experiments were carried out in the same solvent. All calculations performed by Gaussian09 program.[S9-10] Graphical structures are visualized with CYLview.[S11]

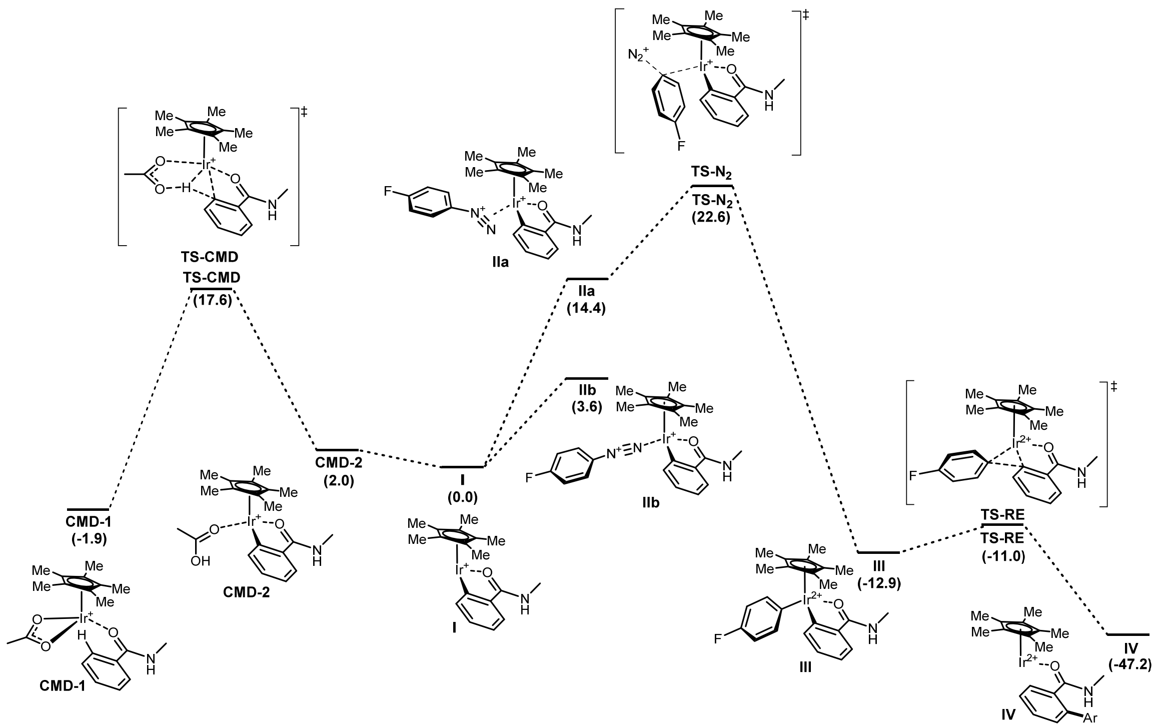


Figure S5. Potential Energy Surface of Full Catalytic Cycle of the Ir-Catalyzed C–H Arylation

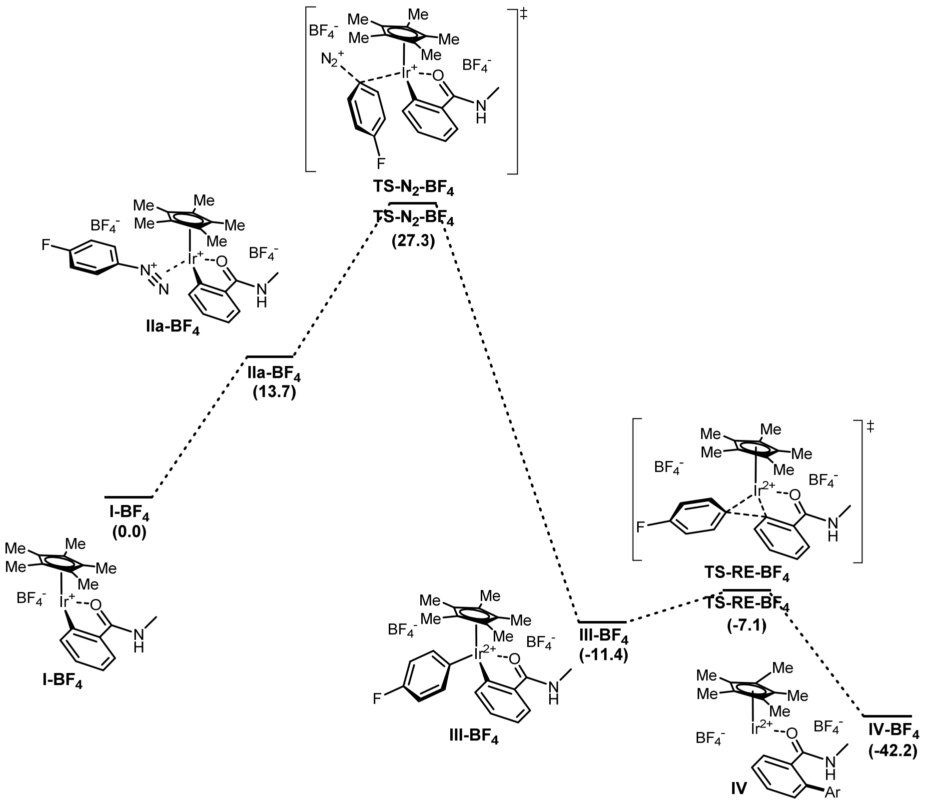
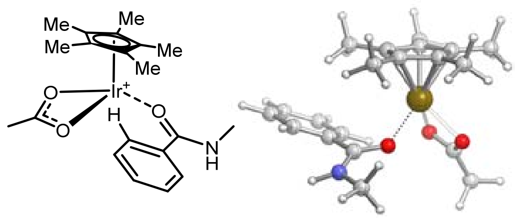


Figure S6. Potential Energy Surface for the Formation of Carbon-Aryl Bond from an Iridacyclic Intermediate I (Counteranion (BF_4^-) Included)

2. Cartesian Coordinates of Optimized Structures and Geometries of Stationary and Transition States

2.1 Cartesian Coordinates of Optimized Structures and Geometries of Stationary and Transition States in Figure S5

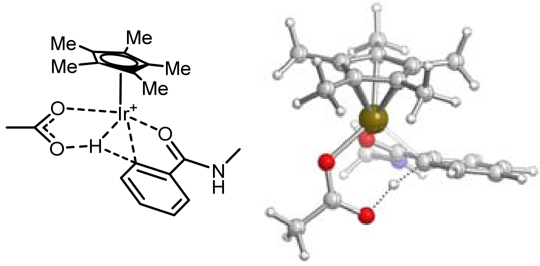
CMD-1



Ir	-0.34568	-0.15627	0.38651
O	1.30386	-1.46587	0.04069

C	1.61277	-1.62073	-1.19035
C	0.00222	0.10893	-1.61770
C	0.96887	-0.75455	-2.17208
C	-0.33632	1.03652	-3.82819
C	-0.65096	0.99562	-2.47174
H	-1.40864	1.67613	-2.08089
C	-1.69819	-0.40582	2.30165
C	-1.32862	-1.67070	1.79771
C	-2.52174	-0.55396	0.10669
C	-2.37842	0.32068	1.23296
C	-1.78809	-1.75763	0.40754
N	2.50136	-2.54901	-1.50795
C	1.28609	-0.71303	-3.53420
H	2.04512	-1.36879	-3.95985
C	0.63242	0.18639	-4.36139
H	0.87525	0.22725	-5.42027
C	3.11194	-3.41993	-0.51574
H	3.75683	-4.13253	-1.03116
H	3.71058	-2.83734	0.19256
H	2.33887	-3.96482	0.03777
H	2.73764	-2.68418	-2.48288
H	-0.85428	1.73968	-4.47780
C	-1.50353	0.09167	3.68865
H	-1.31455	1.17036	3.73485
H	-2.41789	-0.08936	4.27083
H	-0.68921	-0.42729	4.20673
C	-3.04563	1.64378	1.36156
H	-2.97694	2.22356	0.43288
H	-4.11216	1.49304	1.57798
H	-2.63612	2.24683	2.17861
C	-3.34235	-0.30201	-1.10268
H	-2.93606	-0.79569	-1.99143
H	-4.35108	-0.70267	-0.92982
H	-3.44669	0.76697	-1.31524
C	-1.70150	-2.97297	-0.44395
H	-0.78198	-3.53745	-0.24715
H	-2.54952	-3.63676	-0.22533
H	-1.73577	-2.72645	-1.51105
C	-0.58358	-2.75055	2.49321
H	-1.25343	-3.59645	2.69836
H	0.23781	-3.12463	1.86924
H	-0.16349	-2.41425	3.44635
C	2.50619	1.32499	0.15714
C	2.47045	2.16898	-0.90800
C	1.35232	3.01936	-1.10093
C	0.26867	3.03651	-0.26449
C	0.20703	2.11877	0.80461
C	1.35026	1.26292	1.01514
H	3.36676	0.69592	0.36861
H	3.30212	2.22917	-1.60474
H	-0.53290	3.75452	-0.41713
H	-0.46931	2.32636	1.62923
N	1.60193	0.82457	2.30794
N	1.84414	0.47142	3.33866
F	1.39825	3.85149	-2.12209

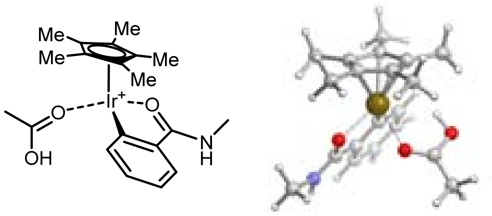
TS-CMD



Ir	-0.44031	-0.41198	-0.58959
O	1.62350	-1.15221	-0.72868
C	2.16024	-0.96976	-1.85734
C	0.47113	0.71510	-2.29624
C	1.46623	-0.12803	-2.84953
C	0.03372	1.54852	-4.53746
C	-0.22009	1.56568	-3.16890
H	-0.95181	2.26385	-2.76204
C	-2.41446	-0.58785	0.30656
C	-1.69124	-1.82535	0.49073
C	-1.91120	-1.44524	-1.81226
C	-2.54468	-0.34379	-1.10439
C	-1.39654	-2.35296	-0.82415
N	3.33762	-1.52294	-2.13337
C	1.71468	-0.15999	-4.21777
H	2.44094	-0.85022	-4.64586
C	0.98735	0.67705	-5.06122
H	1.17108	0.65169	-6.13296
C	4.03613	-2.37206	-1.18446
H	4.84133	-2.89185	-1.70674
H	4.45761	-1.78289	-0.36164
H	3.33886	-3.10612	-0.76861
H	3.81146	-1.25503	-2.98684
H	-0.51334	2.21419	-5.20212
C	-2.92633	0.28185	1.39640
H	-3.08154	1.31033	1.05311
H	-3.88994	-0.10230	1.75819
H	-2.23626	0.30904	2.24698
C	-3.30193	0.77482	-1.72644
H	-3.00497	0.93437	-2.76832
H	-4.37630	0.54494	-1.71711
H	-3.15725	1.71692	-1.18469
C	-1.89214	-1.64183	-3.28647
H	-1.05668	-2.27961	-3.59655
H	-2.82304	-2.12094	-3.61845
H	-1.79602	-0.68934	-3.81995
C	-0.62119	-3.58982	-1.09758
H	0.15985	-3.74404	-0.34419
H	-1.28592	-4.46391	-1.08137
H	-0.13784	-3.55011	-2.08056
C	-1.36437	-2.46057	1.79489
H	-2.18779	-3.10927	2.12441
H	-0.45949	-3.07520	1.72964
H	-1.20043	-1.70631	2.57328

H	0.86547	1.32941	-1.22218
C	1.21160	1.66409	0.82579
O	1.56035	2.06774	-0.31474
O	0.39367	0.71041	1.02143
C	1.80397	2.32469	2.03389
H	1.22132	2.10203	2.93097
H	2.82414	1.94665	2.17420
H	1.87134	3.40544	1.87736

CMD-2



Ir	-0.25675	-0.31617	0.09533
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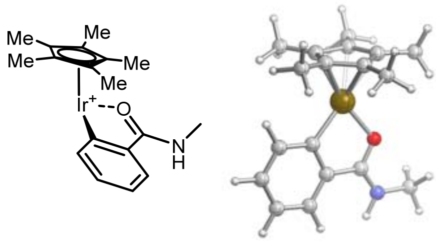
C	2.19361	-0.73525	-1.43286
C	0.50068	0.98147	-1.30544
C	1.70776	0.56227	-1.91106
C	0.62917	2.98959	-2.67718
C	-0.01485	2.21581	-1.71507
H	-0.94107	2.59906	-1.28320
C	-2.24032	0.04218	0.91076
C	-1.74693	-1.12478	1.64346
C	-1.76445	-1.63472	-0.62066
C	-2.34012	-0.31991	-0.48083
C	-1.46527	-2.14557	0.71901
N	3.33335	-1.27091	-1.86440
C	2.35455	1.33443	-2.88106
H	3.27840	0.99681	-3.35152
C	1.81465	2.55175	-3.26631
H	2.31202	3.15608	-4.02140
C	3.81549	-2.55535	-1.39010
H	4.71174	-2.81994	-1.95349
H	4.05899	-2.51191	-0.32227
H	3.05346	-3.32726	-1.54215
H	3.90003	-0.75395	-2.52294
H	0.20041	3.94619	-2.97249
C	-2.82754	1.25478	1.54911
H	-2.81153	2.12506	0.88141
H	-3.87791	1.06815	1.81360
H	-2.30424	1.52362	2.47444
C	-2.96420	0.47868	-1.56740
H	-2.42570	0.36644	-2.51528
H	-3.99709	0.13861	-1.72415
H	-3.00294	1.54609	-1.32358
C	-1.65536	-2.42636	-1.87533
H	-0.74563	-3.03887	-1.87598

H	-2.51559	-3.10201	-1.98095
H	-1.62430	-1.77564	-2.75664
C	-0.89303	-3.49230	0.98391
H	-0.51217	-3.58211	2.00649
H	-1.65776	-4.26771	0.83793
H	-0.06745	-3.71367	0.29572
C	-1.52971	-1.14942	3.11448
H	-2.48645	-1.28092	3.63910
H	-0.86401	-1.96481	3.41576
H	-1.09322	-0.20766	3.47161
H	-0.30426	2.02935	1.06350
C	1.28314	1.61940	1.94957
O	0.30449	2.46447	1.70738
O	1.32778	0.49299	1.44613
C	2.31716	2.12887	2.88512
H	3.11099	1.39097	3.01088
H	2.72919	3.06942	2.50371
H	1.85325	2.34590	3.85420

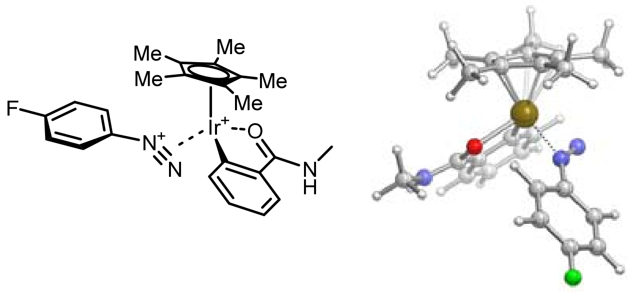
I



Ir	-0.33128	0.06713	-0.05177
O	1.06538	1.64673	0.02053
C	2.28274	1.27004	-0.01250
C	1.42066	-0.98473	-0.01893
C	2.57748	-0.17042	-0.01226
C	2.89608	-2.91766	-0.02467
C	1.61559	-2.36916	-0.02655
H	0.75722	-3.04132	-0.03248
C	-2.34707	0.43820	-0.97012
C	-2.36863	1.03607	0.30961
C	-1.89641	-1.26468	0.57361
C	-2.04009	-0.98877	-0.81933
C	-2.02566	0.00946	1.26812
N	3.23194	2.19131	-0.04921
C	3.86289	-0.71249	-0.00884
H	4.75327	-0.08413	0.00241
C	4.01967	-2.09289	-0.01339
H	5.01749	-2.52561	-0.00761
C	2.94321	3.61628	-0.07681
H	3.88565	4.16079	-0.00383
H	2.43727	3.88817	-1.00978
H	2.29957	3.88855	0.76515
H	4.19903	1.89646	-0.09712
H	3.02148	-3.99916	-0.02854

C	-2.55533	1.10399	-2.27975
H	-1.82705	0.75486	-3.02203
H	-3.55607	0.86704	-2.66849
H	-2.47038	2.19264	-2.20357
C	-2.01143	-1.96814	-1.93648
H	-1.45617	-2.87325	-1.66760
H	-3.03399	-2.26657	-2.20730
H	-1.54200	-1.54045	-2.82995
C	-1.73618	-2.58731	1.23349
H	-0.97946	-2.55472	2.02684
H	-2.68646	-2.89751	1.68912
H	-1.44483	-3.36536	0.51933
C	-1.93282	0.19902	2.73578
H	-1.51457	1.17942	2.99102
H	-2.93746	0.13963	3.17967
H	-1.31375	-0.57432	3.20351
C	-2.58793	2.46974	0.64026
H	-3.59072	2.62334	1.06154
H	-1.86146	2.82157	1.38320
H	-2.49542	3.10843	-0.24452

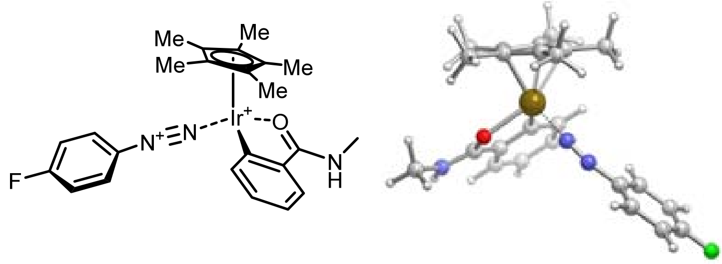
IIa



Ir	0.53809	-0.41729	-0.08497
O	0.02557	1.08189	1.29976
C	0.57226	2.22677	1.09947
C	1.39211	1.24574	-0.92309
C	1.30063	2.41528	-0.14522
C	2.56129	2.50235	-2.60970
C	2.01735	1.29922	-2.16253
H	2.07903	0.41049	-2.79077
C	0.39652	-2.65627	0.65786
C	0.91038	-1.82057	1.67711
C	2.37294	-1.67170	-0.15905
C	1.26020	-2.52145	-0.50202
C	2.12055	-1.15925	1.16444
N	0.43502	3.15442	2.02817
C	1.84760	3.61923	-0.59896
H	1.77371	4.53278	-0.01029
C	2.48193	3.65695	-1.83116
H	2.90788	4.58929	-2.19300
C	-0.29102	2.92069	3.26820
H	-0.30620	3.84896	3.83983
H	-1.31868	2.60975	3.05412

H	0.20270	2.14039	3.85902
H	0.88288	4.05255	1.89101
H	3.04952	2.53983	-3.58160
C	-0.81859	-3.50786	0.71959
H	-1.34180	-3.54162	-0.24284
H	-0.53411	-4.53930	0.96872
H	-1.52515	-3.16267	1.48090
C	1.09540	-3.24307	-1.78804
H	1.53341	-2.68566	-2.62338
H	1.60471	-4.21466	-1.72545
H	0.04238	-3.43676	-2.01876
C	3.59060	-1.43553	-0.97140
H	4.01945	-0.44478	-0.79060
H	4.34702	-2.18250	-0.69336
H	3.40359	-1.54351	-2.04476
C	3.03432	-0.31128	1.97338
H	2.48118	0.28370	2.70942
H	3.73753	-0.95044	2.52412
H	3.61837	0.36968	1.34477
C	0.34975	-1.59130	3.03077
H	1.02841	-2.00206	3.79025
H	0.23986	-0.51698	3.23010
H	-0.62843	-2.06622	3.15143
C	-3.56361	0.17145	-1.87913
C	-4.89516	0.39587	-1.60283
C	-5.31516	0.39291	-0.27179
C	-4.45501	0.17227	0.80085
C	-3.11836	-0.04928	0.53450
C	-2.69448	-0.04676	-0.79893
H	-3.18707	0.16653	-2.89908
H	-5.62027	0.57516	-2.39131
H	-4.84644	0.17867	1.81346
H	-2.39822	-0.23254	1.33095
N	-1.33935	-0.27559	-1.03899
N	-0.59098	-0.42310	-1.95415
F	-6.59221	0.60907	-0.01968

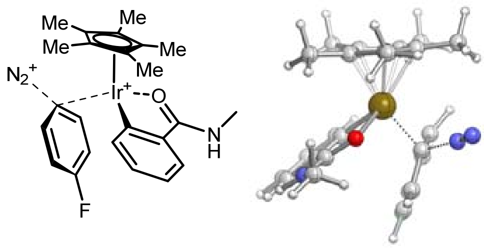
IIb



Ir	-1.21690	-0.40349	1.35314
O	0.63639	-1.46036	1.39755
C	0.87410	-2.16341	0.35750

C	-1.07517	-1.11682	-0.57869
C	0.00493	-1.98932	-0.80372
C	-1.72187	-1.38311	-2.88518
C	-1.92563	-0.80598	-1.63258
H	-2.75049	-0.10747	-1.48917
C	-2.31482	0.10802	3.35192
C	-1.80038	-1.20418	3.42501
C	-3.31147	-1.14465	1.62967
C	-3.18714	0.17941	2.18302
C	-2.36243	-1.98020	2.31446
N	1.89325	-3.00612	0.38386
C	0.20048	-2.57323	-2.05955
H	1.03042	-3.25369	-2.24707
C	-0.66847	-2.27178	-3.09728
H	-0.52028	-2.71974	-4.07676
C	2.72458	-3.18508	1.56381
H	3.46256	-3.95950	1.35262
H	3.23950	-2.25245	1.81696
H	2.10895	-3.49286	2.41671
H	2.08501	-3.57097	-0.43373
H	-2.39123	-1.13351	-3.70632
C	-2.01388	1.24862	4.25463
H	-1.89647	2.18688	3.69949
H	-2.84237	1.39197	4.96188
H	-1.10093	1.08070	4.83410
C	-3.97410	1.37690	1.78482
H	-4.32105	1.31088	0.74839
H	-4.85803	1.47137	2.43015
H	-3.39069	2.29902	1.88916
C	-4.25198	-1.58227	0.57064
H	-3.80399	-2.32142	-0.10239
H	-5.12094	-2.05261	1.05158
H	-4.62204	-0.74397	-0.02752
C	-2.14295	-3.43581	2.09574
H	-1.09877	-3.71637	2.28178
H	-2.76983	-4.02109	2.78187
H	-2.39714	-3.73090	1.07182
C	-0.84148	-1.74994	4.41703
H	-1.34009	-2.51306	5.02992
H	0.01128	-2.23347	3.92411
H	-0.45719	-0.97370	5.08504
C	-0.71565	3.44293	-1.57776
C	-0.59843	4.56970	-2.36266
C	0.19684	5.62329	-1.91201
C	0.88650	5.59489	-0.70261
C	0.78117	4.47226	0.09262
C	-0.02271	3.41388	-0.35400
H	-1.31794	2.59242	-1.88728
H	-1.10699	4.65294	-3.31859
H	1.49143	6.44739	-0.40887
H	1.30076	4.39915	1.04369
N	-0.12852	2.29468	0.43761
N	-0.50238	1.26584	0.76703
F	0.30014	6.69681	-2.67091

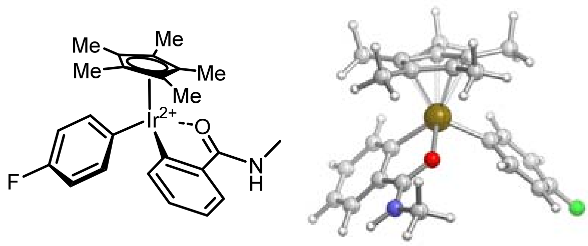
TS-N$_2$



Ir	-0.34605	-0.11235	0.37452
O	1.24008	-1.47719	-0.02004
C	1.52152	-1.63185	-1.25907
C	-0.06334	0.13104	-1.64608
C	0.86803	-0.75469	-2.22263
C	-0.45074	1.06593	-3.83833
C	-0.72190	1.03650	-2.47181
H	-1.45089	1.73364	-2.05866
C	-1.73405	-0.36629	2.25557
C	-1.32690	-1.63547	1.78335
C	-2.54649	-0.60710	0.06452
C	-2.43128	0.30705	1.16839
C	-1.79142	-1.77579	0.39869
N	2.39517	-2.56623	-1.59483
C	1.13743	-0.72402	-3.59487
H	1.86597	-1.39839	-4.04354
C	0.47552	0.18873	-4.40100
H	0.68146	0.22028	-5.46791
C	3.03063	-3.43595	-0.61633
H	3.77004	-4.05042	-1.13117
H	3.52876	-2.83963	0.15456
H	2.29005	-4.08687	-0.13665
H	2.60334	-2.70892	-2.57525
H	-0.97122	1.78161	-4.47167
C	-1.57232	0.18021	3.62840
H	-1.33481	1.25130	3.63917
H	-2.51947	0.06959	4.17455
H	-0.80390	-0.35153	4.19890
C	-3.13833	1.61130	1.25867
H	-3.05856	2.18459	0.32702
H	-4.20613	1.42896	1.44301
H	-2.77095	2.23262	2.08169
C	-3.35576	-0.39305	-1.15990
H	-2.93894	-0.90832	-2.03116
H	-4.36483	-0.79240	-0.98646
H	-3.46236	0.66912	-1.40378
C	-1.65917	-3.01066	-0.41680
H	-0.69867	-3.50815	-0.23779
H	-2.45302	-3.71956	-0.14462
H	-1.74777	-2.80417	-1.48913
C	-0.57398	-2.68629	2.51344
H	-1.22896	-3.54669	2.70691
H	0.27602	-3.04787	1.92084
H	-0.19429	-2.32898	3.47558

C	2.42650	1.25344	0.21213
C	2.49505	2.16089	-0.79935
C	1.42089	3.06577	-1.03498
C	0.28679	3.09333	-0.27904
C	0.14325	2.13334	0.76014
C	1.18240	1.16743	0.91680
H	3.23545	0.55843	0.42190
H	3.36949	2.21409	-1.44318
H	-0.47087	3.85646	-0.43574
H	-0.53992	2.35411	1.57613
N	1.61419	0.86507	2.58579
N	1.95538	0.35432	3.50712
F	1.58464	3.94094	-2.01182

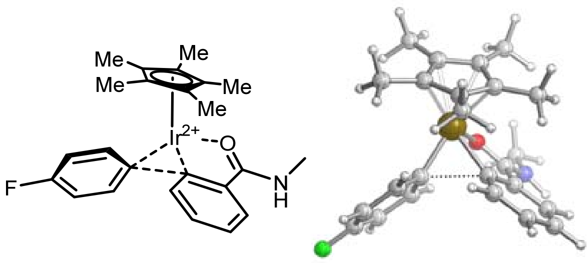
III



Ir	-0.44823	-0.09414	-0.09970
O	1.22803	-1.29180	-0.57426
C	1.37125	-1.57748	-1.81144
C	-0.57096	-0.20874	-2.11546
C	0.45515	-0.94066	-2.75185
C	-1.35735	0.51272	-4.27616
C	-1.48662	0.50327	-2.88850
H	-2.28955	1.06996	-2.41996
C	-1.59528	0.06443	1.90902
C	-1.02181	-1.23125	1.69733
C	-2.63046	-0.86934	0.02866
C	-2.55418	0.30691	0.85713
C	-1.66743	-1.81279	0.51233
N	2.32304	-2.41846	-2.16642
C	0.56766	-0.94536	-4.13726
H	1.37205	-1.47878	-4.64102
C	-0.34640	-0.21848	-4.89626
H	-0.26242	-0.21598	-5.97992
C	3.21718	-3.03502	-1.19604
H	3.92950	-3.66195	-1.73265
H	3.75842	-2.26338	-0.63872
H	2.64621	-3.64976	-0.49120
H	2.41249	-2.67063	-3.14360
H	-2.05710	1.08818	-4.87772
C	-1.33180	0.96210	3.05917
H	-1.38097	2.02111	2.78651
H	-2.10031	0.78765	3.82464
H	-0.35439	0.77251	3.51363
C	-3.41513	1.50571	0.72978

H	-3.63530	1.74840	-0.31578
H	-4.37585	1.31004	1.22842
H	-2.97434	2.38622	1.20730
C	-3.60872	-1.11437	-1.05817
H	-3.18987	-1.72987	-1.86181
H	-4.46565	-1.65661	-0.63402
H	-3.99592	-0.18756	-1.49249
C	-1.44854	-3.18898	0.00696
H	-0.42086	-3.52960	0.17558
H	-2.11418	-3.87837	0.54570
H	-1.67528	-3.26998	-1.06163
C	-0.04621	-1.93956	2.55964
H	-0.58268	-2.64153	3.21355
H	0.66416	-2.52487	1.96447
H	0.51979	-1.24896	3.19201
C	2.23186	0.75396	1.08103
C	3.16718	1.75380	1.26417
C	2.76328	3.08628	1.14930
C	1.45114	3.45505	0.89157
C	0.50446	2.44814	0.76091
C	0.90882	1.10023	0.75647
H	2.53563	-0.28768	1.15010
H	4.20662	1.53097	1.49071
H	1.17969	4.50596	0.84548
H	-0.53939	2.72865	0.61770
F	3.66922	4.03442	1.32536

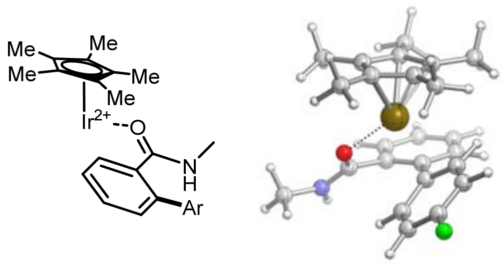
TS-RE



Ir	-0.24176	-0.47499	-0.24030
O	-0.77958	1.10403	-1.54378
C	-0.96141	2.23408	-0.97826
C	-0.01695	1.21647	1.01470
C	-0.61255	2.35549	0.43641
C	0.10966	2.36791	3.12177
C	0.37801	1.24251	2.34301
H	0.89353	0.39944	2.79486
C	-0.35206	-2.61241	0.33149
C	-1.28893	-2.43450	-0.78568
C	-1.99805	-1.09346	0.95528
C	-0.82944	-1.83974	1.42603
C	-2.30060	-1.52784	-0.39292
N	-1.44060	3.23847	-1.68892
C	-0.88347	3.47131	1.23219

H	-1.40123	4.33507	0.81799
C	-0.52950	3.47580	2.57374
H	-0.74738	4.34403	3.18943
C	-1.80504	3.10507	-3.09234
H	-2.39184	3.97870	-3.37890
H	-0.91055	3.04312	-3.72173
H	-2.40378	2.20025	-3.23231
H	-1.50857	4.15372	-1.26024
H	0.40950	2.37224	4.16719
C	0.77466	-3.57842	0.32718
H	1.43102	-3.44984	1.19284
H	0.37722	-4.60237	0.35467
H	1.38076	-3.48327	-0.58158
C	-0.37752	-1.94497	2.83530
H	-0.68545	-1.09091	3.44396
H	-0.84522	-2.84108	3.26741
H	0.70559	-2.08041	2.93019
C	-2.85618	-0.20488	1.77490
H	-3.31634	0.58478	1.17023
H	-3.66834	-0.80258	2.21323
H	-2.30445	0.26739	2.59379
C	-3.41637	-1.02464	-1.23016
H	-3.15566	-1.02438	-2.29381
H	-4.29766	-1.66675	-1.09847
H	-3.70497	-0.00532	-0.95039
C	-1.13558	-3.09788	-2.09974
H	-1.42579	-4.15527	-2.00797
H	-1.76313	-2.64169	-2.87067
H	-0.09259	-3.08321	-2.43971
C	2.15040	0.87440	-1.14181
C	3.50341	0.86986	-1.45604
C	4.37784	0.20797	-0.61006
C	3.95070	-0.46638	0.53947
C	2.60625	-0.47985	0.83615
C	1.68324	0.12471	-0.04179
H	1.46461	1.41621	-1.78545
H	3.88555	1.39680	-2.32601
H	4.68175	-0.96132	1.17311
H	2.26963	-0.99620	1.73262
F	5.67076	0.22464	-0.88123

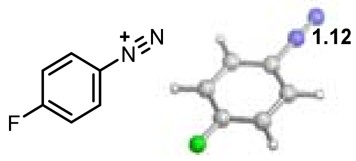
IV



Ir	-0.09412	-0.45859	0.16738
O	0.85203	0.91746	1.55932

C	1.78971	1.53870	0.98289
C	0.88608	1.25115	-1.35473
C	2.00628	1.31414	-0.46881
C	2.42132	0.59953	-3.13244
C	1.14217	0.89923	-2.69424
H	0.32262	0.90549	-3.40995
C	-1.62185	-2.04941	0.19217
C	-0.93704	-1.94759	1.46517
C	0.64174	-2.47405	-0.16884
C	-0.64647	-2.33802	-0.82141
C	0.46640	-2.23404	1.24316
N	2.57149	2.36730	1.64932
C	3.29101	1.02089	-0.92683
H	4.12613	1.03884	-0.22871
C	3.50017	0.66172	-2.25134
H	4.50420	0.42969	-2.59722
C	2.40505	2.61408	3.07572
H	3.23774	3.22739	3.42039
H	1.46169	3.13922	3.26241
H	2.39903	1.66499	3.62004
H	3.27152	2.89214	1.13596
H	2.58238	0.33572	-4.17457
C	-3.08215	-1.87761	0.01708
H	-3.37253	-1.81529	-1.03561
H	-3.59683	-2.74223	0.45902
H	-3.44367	-0.98088	0.53566
C	-0.90159	-2.61686	-2.25813
H	-0.08445	-2.25751	-2.89424
H	-0.97867	-3.70278	-2.40638
H	-1.83683	-2.17059	-2.61100
C	1.91116	-2.79051	-0.86079
H	2.78533	-2.53096	-0.25554
H	1.95140	-3.86968	-1.06678
H	1.98448	-2.26849	-1.82295
C	1.53258	-2.24829	2.27523
H	1.28898	-1.58434	3.11161
H	1.65858	-3.26408	2.67246
H	2.49347	-1.92539	1.85764
C	-1.56875	-1.65629	2.77393
H	-1.75654	-2.59687	3.31019
H	-0.91921	-1.03782	3.40376
H	-2.52614	-1.13900	2.65422
C	-0.76916	2.67873	-0.02906
C	-2.05671	3.05489	0.26732
C	-3.11965	2.38647	-0.34855
C	-2.92245	1.36948	-1.25996
C	-1.61541	0.98759	-1.55603
C	-0.50277	1.60619	-0.92787
H	0.05290	3.24203	0.40765
H	-2.26623	3.87686	0.94622
H	-3.77382	0.90291	-1.74737
H	-1.45256	0.24174	-2.33129
F	-4.35337	2.76545	-0.05840

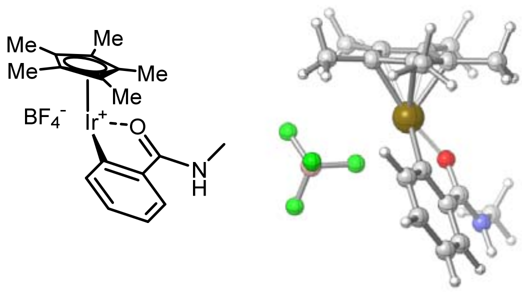
Aryldiazonium Salt 2a (BF_4^- omitted)



C	0.34195	-1.24109	-0.00016
C	-1.03376	-1.22934	0.00002
C	-1.69474	-0.00030	0.00007
C	-1.03477	1.22912	-0.00003
C	0.34109	1.24230	-0.00011
C	1.00188	0.00114	-0.00001
H	0.90671	-2.16836	-0.00028
H	-1.61048	-2.14901	0.00003
H	-1.61197	2.14849	-0.00002
H	0.90449	2.17037	-0.00022
N	2.36849	0.00012	0.00005
N	3.48212	-0.00081	0.00011
F	-3.00810	-0.00085	0.00007

2.2 Cartesian Coordinates of Optimized Structures and Geometries of Stationary and Transition States in Figure S6

I-BF_4



Ir	-1.24243	-0.83292	1.47145
O	0.62821	-1.90198	1.46606
C	0.98794	-2.32116	0.32572
C	-1.03364	-1.30954	-0.50171
C	0.12163	-2.05434	-0.82546
C	-1.59660	-1.33558	-2.86664
C	-1.87405	-0.94819	-1.55952
H	-2.75144	-0.33159	-1.36276
C	-2.16526	0.03560	3.39741

C	-1.92469	-1.33272	3.58795
C	-3.35609	-1.11147	1.72880
C	-2.99797	0.19474	2.20146
C	-2.59148	-2.06718	2.50729
N	2.14144	-2.97774	0.21408
C	0.40371	-2.44861	-2.13824
H	1.29319	-3.03092	-2.38058
C	-0.46266	-2.09550	-3.16097
H	-0.25395	-2.40059	-4.18416
C	3.01046	-3.21548	1.35146
H	3.85601	-3.82236	1.02332
H	3.38387	-2.26969	1.76112
H	2.47023	-3.74760	2.14209
H	2.43785	-3.29983	-0.69736
H	-2.26919	-1.03980	-3.67114
C	-1.62222	1.17815	4.17927
H	-1.16252	1.91814	3.51240
H	-2.42892	1.68423	4.72863
H	-0.87036	0.85323	4.90659
C	-3.53560	1.49769	1.72728
H	-3.84058	1.44917	0.67631
H	-4.40871	1.79130	2.32784
H	-2.77565	2.28168	1.81149
C	-4.36046	-1.44873	0.68731
H	-4.05046	-2.30854	0.08216
H	-5.31382	-1.70603	1.16984
H	-4.55093	-0.60779	0.01144
C	-2.66399	-3.55002	2.40508
H	-1.69900	-4.01067	2.65126
H	-3.41401	-3.95167	3.10138
H	-2.93805	-3.86583	1.39153
C	-1.06969	-1.97980	4.61813
H	-1.68627	-2.55180	5.32539
H	-0.36358	-2.68336	4.15822
H	-0.49071	-1.24572	5.18845
B	-0.15652	2.14951	0.48298
F	-0.48062	2.90212	1.60544
F	-1.25306	1.99334	-0.33807
F	0.91785	2.68470	-0.19025
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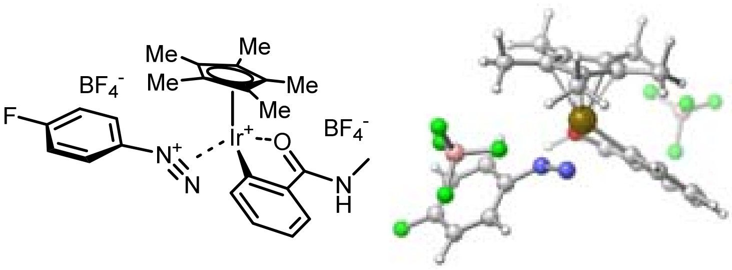
IIa-BF$_4$



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C	0.27863	-2.14582	-0.64107
C	-0.90773	-0.99347	-2.86161
C	-1.20328	-0.49450	-1.59390
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C	-2.31641	-0.20383	3.39636
C	-1.95243	-1.56733	3.30216
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C	-3.00826	0.15468	2.16980
C	-2.42671	-2.08373	2.00810
N	1.71630	-3.61120	0.69556
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C	-0.04825	-2.08105	-3.01900
H	0.15639	-2.47354	-4.01239
C	2.26410	-4.05402	1.96581
H	2.91289	-4.90942	1.77271
H	2.84171	-3.25167	2.43585
H	1.46431	-4.36506	2.64861
H	1.80921	-4.24777	-0.10295
H	-1.36037	-0.53139	-3.73726
C	-2.02230	0.74472	4.49963
H	-1.68602	1.71391	4.11325
H	-2.93442	0.91980	5.08732
H	-1.25053	0.36046	5.17461
C	-3.55986	1.49918	1.86930
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H	-5.00518	-1.46536	0.42969
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H	-3.23892	-4.04710	1.93794
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H	-0.33019	-2.85979	3.80881
H	-0.82399	-1.76110	5.11587
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C	3.56244	2.39435	3.72682
C	3.02413	1.15160	4.04860
C	1.92967	0.70846	3.33418
C	1.41693	1.52985	2.32545
H	1.50338	3.39671	1.23611
H	3.51556	4.17842	2.53228
H	3.46801	0.56295	4.84571
H	1.46610	-0.25478	3.54105
N	0.29262	1.07807	1.64150
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F	4.61152	2.82097	4.41343
B	-0.38653	4.05338	3.83496
F	-1.35991	4.67435	4.60485
F	-1.01915	3.34250	2.77925

F	0.47754	4.99213	3.28010
F	0.32851	3.13623	4.60728
B	0.38800	-6.20221	-0.58437
F	0.68307	-6.45525	0.75136
F	-0.65111	-5.27923	-0.67602
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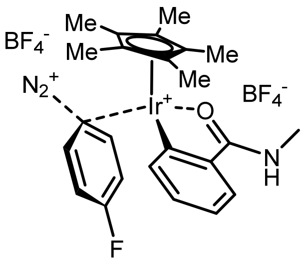
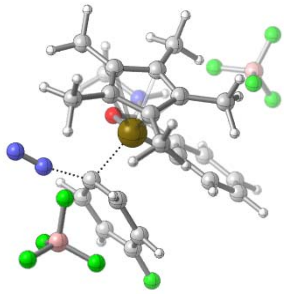
TS-N_2-BF_4





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C	2.02854	1.17664	0.54392
C	1.95362	2.81291	-1.68423
C	0.98795	1.82126	-1.52796
H	0.21493	1.70598	-2.28794
C	-1.32829	-2.56222	-0.58500
C	-0.13396	-2.81619	0.12636
C	0.44706	-1.63778	-1.81289
C	-0.98983	-1.74259	-1.73912
C	0.97851	-2.21737	-0.61706
N	2.93081	0.14273	2.55597
C	2.99688	2.17189	0.38582
H	3.78409	2.30540	1.12510
C	2.95254	2.99279	-0.72882
H	3.70404	3.76740	-0.86175
C	2.85442	-0.77146	3.68087
H	2.89399	-1.81869	3.35247
H	3.69577	-0.57340	4.34745
H	1.91981	-0.61040	4.22508
H	3.85090	0.41497	2.21330
H	1.92374	3.45414	-2.56374
C	-2.68077	-3.09717	-0.29097
H	-3.47148	-2.36074	-0.46812
H	-2.87542	-3.94735	-0.96027
H	-2.76413	-3.47094	0.73543
C	-1.94686	-1.31885	-2.79495
H	-1.62965	-0.38442	-3.27400
H	-2.00077	-2.09306	-3.57329

H	-2.95898	-1.18112	-2.39530
C	1.24063	-1.09085	-2.94121
H	2.22594	-0.73570	-2.61687
H	1.39397	-1.89302	-3.67734
H	0.72213	-0.27396	-3.45536
C	2.41538	-2.36657	-0.26668
H	2.54916	-2.49844	0.81377
H	2.81850	-3.26520	-0.75496
H	3.01906	-1.50910	-0.58947
C	0.02294	-3.56414	1.39952
H	0.51397	-4.52936	1.21506
H	0.64917	-3.00408	2.10544
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C	-1.36138	1.48781	2.07711
C	-1.18927	2.77985	1.69074
C	-1.47309	3.17570	0.35233
C	-1.92244	2.31715	-0.60276
C	-2.06952	0.94147	-0.26692
C	-1.69626	0.55080	1.04828
H	-1.16905	1.15417	3.09274
H	-0.84387	3.53372	2.39381
H	-2.23364	2.67984	-1.57811
H	-2.76619	0.33839	-0.84320
N	-2.88527	-0.55082	1.76253
N	-3.46329	-1.38737	2.19665
F	-1.33230	4.46567	0.07306
B	-5.21310	0.66114	-0.39755
B	5.39827	0.16470	-0.61518
F	-6.58224	0.51020	-0.31599
F	-4.85923	1.52304	-1.43000
F	-4.69573	1.13774	0.81550
F	6.41526	-0.71633	-0.95860
F	4.98155	-0.11045	0.71003
F	5.84516	1.47746	-0.68725
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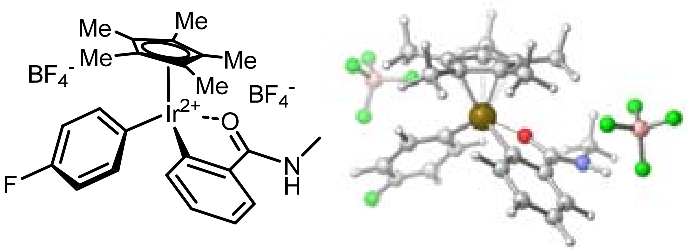
III-BF$_4$



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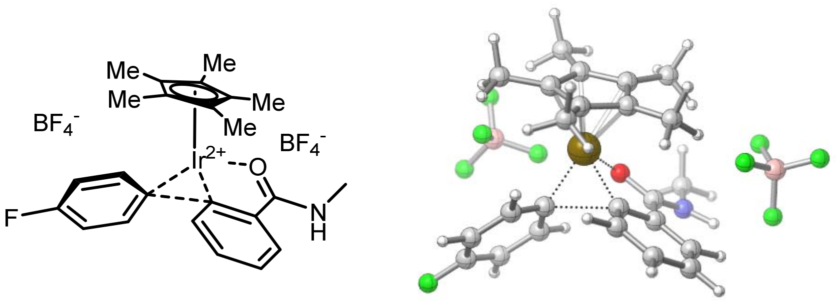
C	0.30939	-0.83136	-2.83936

C	-1.44083	0.79332	-4.25432
C	-1.51005	0.76924	-2.86311
H	-2.24179	1.39039	-2.34760
C	-1.61813	0.16013	1.79978
C	-0.93762	-1.09623	1.67168
C	-2.52304	-0.95803	-0.05186
C	-2.56127	0.26533	0.71010
C	-1.50843	-1.78946	0.51027
N	1.99531	-2.53315	-2.36931
C	0.35744	-0.82536	-4.22904
H	1.06956	-1.44849	-4.76367
C	-0.52179	-0.00797	-4.93134
H	-0.48975	0.00706	-6.01807
C	2.81269	-3.29961	-1.44487
H	3.47673	-3.94317	-2.02455
H	3.41108	-2.62522	-0.82610
H	2.18168	-3.92166	-0.79820
H	1.74975	-2.96946	-3.26340
H	-2.11586	1.43592	-4.81557
C	-1.46972	1.11141	2.92680
H	-1.80610	2.12110	2.66912
H	-2.10501	0.76364	3.75418
H	-0.44033	1.17080	3.29687
C	-3.51358	1.38055	0.49630
H	-3.78801	1.49394	-0.55774
H	-4.43904	1.17249	1.05271
H	-3.12167	2.33626	0.85813
C	-3.40666	-1.33320	-1.18362
H	-2.88935	-1.97999	-1.90165
H	-4.27004	-1.88634	-0.78784
H	-3.79450	-0.46012	-1.71814
C	-1.14549	-3.15212	0.06279
H	-0.12463	-3.41668	0.35838
H	-1.82548	-3.87215	0.54189
H	-1.23499	-3.27678	-1.02188
C	0.07350	-1.66488	2.59658
H	-0.41823	-2.35307	3.29915
H	0.82952	-2.24123	2.04847
H	0.58225	-0.88118	3.16863
C	2.34161	0.89424	0.79575
C	3.26035	1.89543	1.02066
C	2.80182	3.20609	1.16339
C	1.46027	3.55249	1.08274
C	0.53792	2.53629	0.90182
C	0.97359	1.21402	0.66540
H	2.67154	-0.13750	0.70138
H	4.32379	1.69164	1.11501
H	1.15766	4.58651	1.22261
H	-0.52259	2.78291	0.89998
F	3.68902	4.15857	1.39900
B	1.85020	2.05108	4.61351
F	0.60294	2.65238	4.79232
F	2.71838	2.94117	3.97816
F	2.37498	1.67089	5.84453
F	1.69052	0.90197	3.80761
B	-0.41933	-4.29672	-3.54629
F	-1.26153	-3.21922	-3.22417

F	0.60918	-3.81705	-4.40633
F	0.17765	-4.77736	-2.38338
F	-1.13128	-5.28809	-4.18883

TS-RE-BF$_4$



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C	1.76340	-1.47675	-1.59145
C	0.28787	0.45081	-1.82066
C	1.02366	-0.56500	-2.46728
C	-0.47033	1.24229	-3.96222
C	-0.43613	1.36380	-2.57492
H	-0.97271	2.18198	-2.10222
C	-1.51812	0.25942	1.75595
C	-1.00271	-1.11194	1.88248
C	-1.88635	-0.86565	-0.23826
C	-2.07508	0.40486	0.45554
C	-1.28034	-1.80819	0.67896
N	2.52052	-2.45676	-2.04211
C	0.96377	-0.68461	-3.85784
H	1.45207	-1.52126	-4.35358
C	0.21966	0.21715	-4.60351
H	0.17348	0.11873	-5.68502
C	3.17109	-3.39178	-1.13864
H	3.64559	-4.16706	-1.74203
H	3.92707	-2.87730	-0.53745
H	2.43525	-3.85957	-0.47556
H	2.40586	-2.75859	-3.01119
H	-1.04586	1.96053	-4.54232
C	-1.52227	1.24685	2.85899
H	-1.73811	2.25945	2.50366
H	-2.30254	0.96698	3.58182
H	-0.55751	1.25194	3.37742
C	-2.89915	1.54105	-0.03069
H	-2.85242	1.66045	-1.11771
H	-3.94922	1.34843	0.22963
H	-2.61997	2.48996	0.43958
C	-2.42199	-1.22316	-1.57241
H	-1.75399	-1.89772	-2.12009
H	-3.37640	-1.74952	-1.42235

H	-2.61957	-0.34228	-2.18976
C	-0.90958	-3.20015	0.32713
H	-0.14235	-3.59326	1.00191
H	-1.79508	-3.84635	0.40853
H	-0.54468	-3.27995	-0.70719
C	-0.34199	-1.63839	3.10055
H	-1.10376	-1.85576	3.86367
H	0.20413	-2.56548	2.89728
H	0.36054	-0.91264	3.52666
C	2.51248	1.56606	-0.11777
C	3.28512	2.66387	0.23604
C	2.65537	3.87693	0.45642
C	1.27375	4.04236	0.33492
C	0.50924	2.94880	-0.01164
C	1.11170	1.68533	-0.16820
H	2.99366	0.60779	-0.27858
H	4.36443	2.58830	0.33667
H	0.83097	5.01932	0.51029
H	-0.56716	3.06786	-0.11950
F	3.38866	4.93404	0.78035
B	0.42810	-4.32166	-3.45140
F	1.51916	-3.80794	-4.21262
F	0.93085	-4.92815	-2.30663
F	-0.38421	-3.23758	-3.07637
F	-0.28510	-5.21426	-4.22295
B	2.66608	0.38627	3.25251
F	2.83778	-0.44226	2.13718
F	2.43167	-0.39885	4.38291
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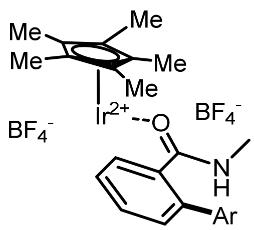
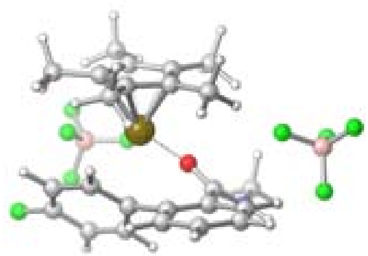
F	1.53594	1.20865	3.04002

IV-BF_4





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O	0.91460	-0.84545	-0.35991
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C	0.15423	1.36681	-2.12923
C	0.40899	0.04010	-2.53769
C	-1.05382	1.73209	-4.20014
C	-0.57539	2.19914	-2.97897
H	-0.74702	3.23528	-2.69026
C	-2.15989	0.77073	2.02939
C	-1.62828	-0.55482	2.29975
C	-2.42273	-0.54303	0.10977
C	-2.68482	0.76491	0.69829
C	-1.78296	-1.36185	1.12169

N	1.98611	-1.75000	-2.08620
C	-0.06514	-0.41979	-3.76673
H	0.10044	-1.45641	-4.05440
C	-0.79619	0.42502	-4.59581
H	-1.17286	0.05366	-5.54615
C	2.59297	-2.74974	-1.22256
H	3.23906	-3.38169	-1.83459
H	3.18523	-2.25949	-0.44379
H	1.82042	-3.37338	-0.75849
H	1.97513	-1.94434	-3.08348
H	-1.62387	2.39790	-4.84455
C	-2.18849	1.87510	3.02202
H	-2.47634	2.82871	2.56794
H	-2.91485	1.64649	3.81359
H	-1.20060	1.98807	3.48284
C	-3.42435	1.85311	0.01257
H	-3.11437	1.96309	-1.03454
H	-4.49432	1.60275	0.00860
H	-3.31140	2.81836	0.51657
C	-2.84578	-0.99619	-1.23638
H	-2.14282	-1.71726	-1.67176
H	-3.82439	-1.49087	-1.14860
H	-2.96333	-0.15513	-1.92834
C	-1.35011	-2.77001	0.94777
H	-0.49311	-3.00516	1.58924
H	-2.17245	-3.44588	1.21951
H	-1.06652	-2.97458	-0.09124
C	-1.02465	-0.99106	3.57592
H	-1.81540	-1.41660	4.21096
H	-0.26225	-1.75927	3.41672
H	-0.55832	-0.15577	4.10204
C	2.06343	1.82904	-0.53161
C	2.58872	2.48647	0.55232
C	1.74710	3.27565	1.34754
C	0.41403	3.44417	1.06291
C	-0.12985	2.75584	-0.03392
C	0.67468	1.91382	-0.84252
H	2.71762	1.24282	-1.17492
H	3.64181	2.41726	0.80714
H	-0.20156	4.09025	1.68313
H	-1.14960	2.97572	-0.34262
F	2.27561	3.90532	2.38721
B	0.03526	-4.09631	-3.10058
F	0.89461	-3.43596	-4.01214
F	0.78140	-4.95466	-2.30703
F	-0.56830	-3.11351	-2.27885
F	-0.94108	-4.78092	-3.79845
B	2.06287	0.46187	3.44267
F	2.01732	-0.61504	2.55103
F	1.96994	0.00120	4.75018
F	3.23196	1.18907	3.25965
F	0.95121	1.30675	3.17982

3. Relaxed PES Scanning to Find Out the Oxidized Structure of Complex IIb

To find out the optimized geometry for the oxidized structure of complex **IIb**, the iridium-aryldiazenide intermediate which could be generated via the oxidation of the iridium metal center by the aryldiazonium moiety, relaxed PES scanning was conducted as a function of Ir-N_{α} distance of the iridacycle **IIb** at every 0.05 Å interval from 1.53 to 1.93 Å to explore the local minimum (calculated by M06/6-31G*//LANL2DZ method, ModRedundant option in Gaussian 09). However, it was observed that no stationary structure was obtained from relaxed PES scanning. Instead, all of the initially guessed structures drifted down to the original **IIb** structure.

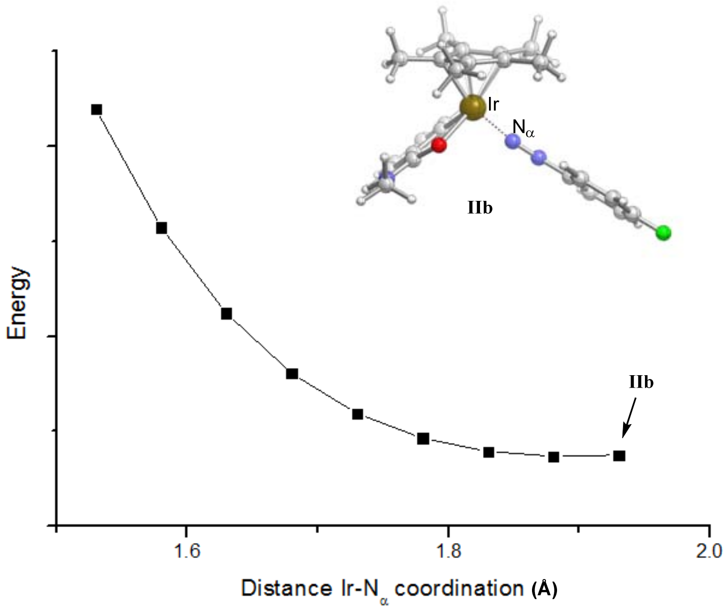

Figure S7. Relaxed PES scanning as a function of Ir-N_{α} distance of the complex **IIb**

VII. References

[S1] Ryu, J.; Shin, K.; Park, S. H.; Kim, J. Y.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 9904.

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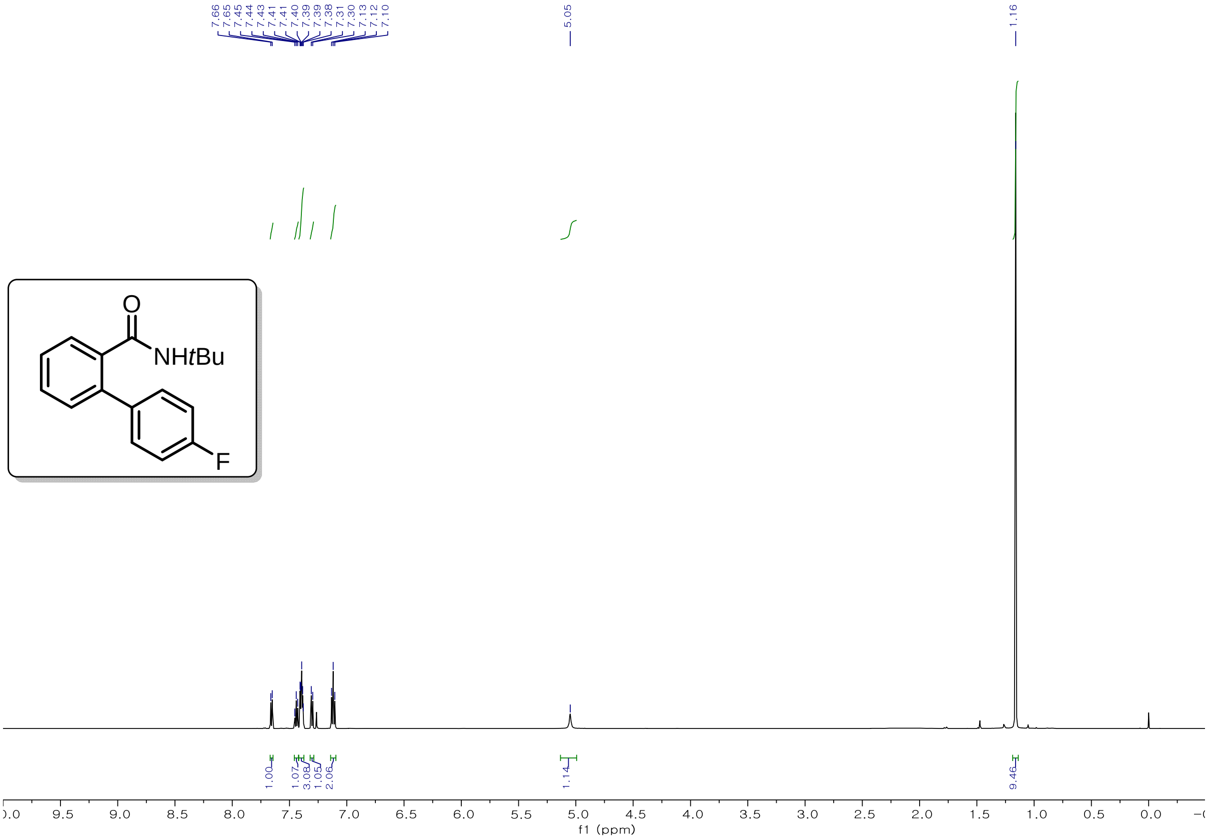
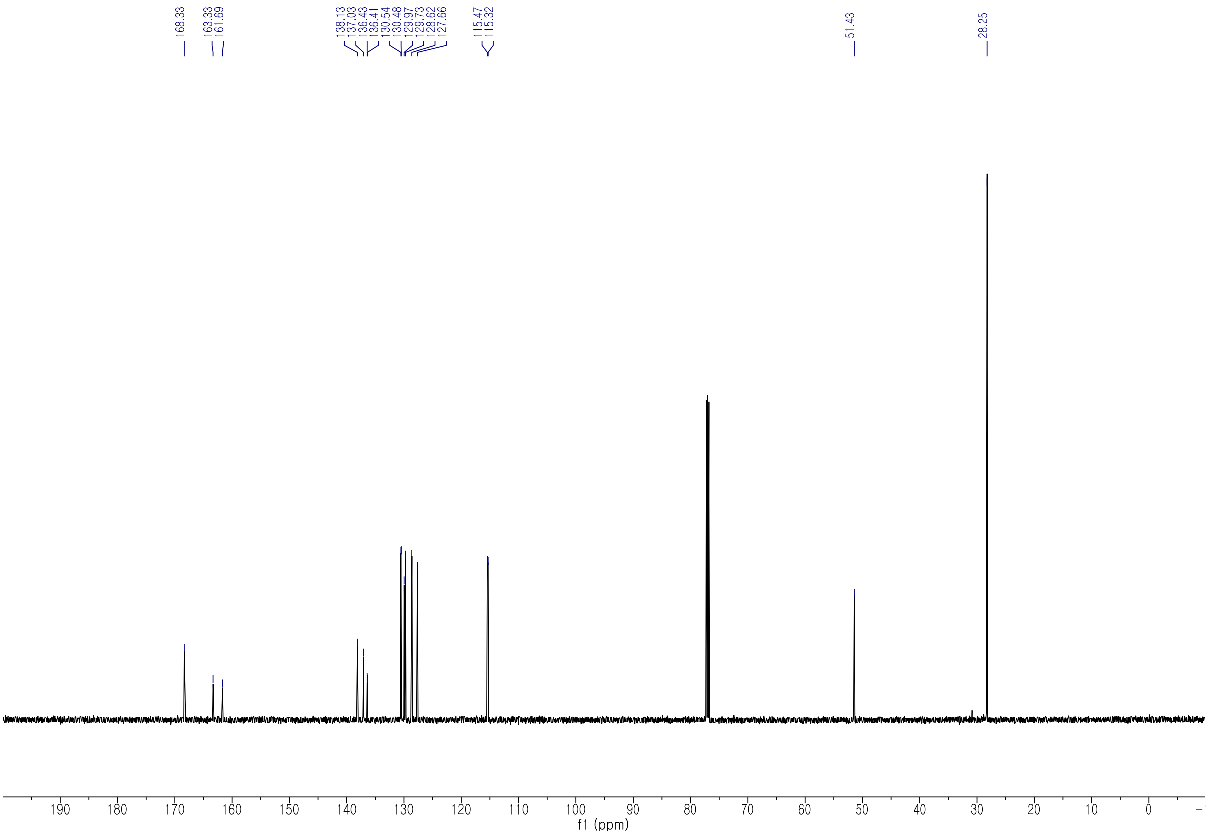
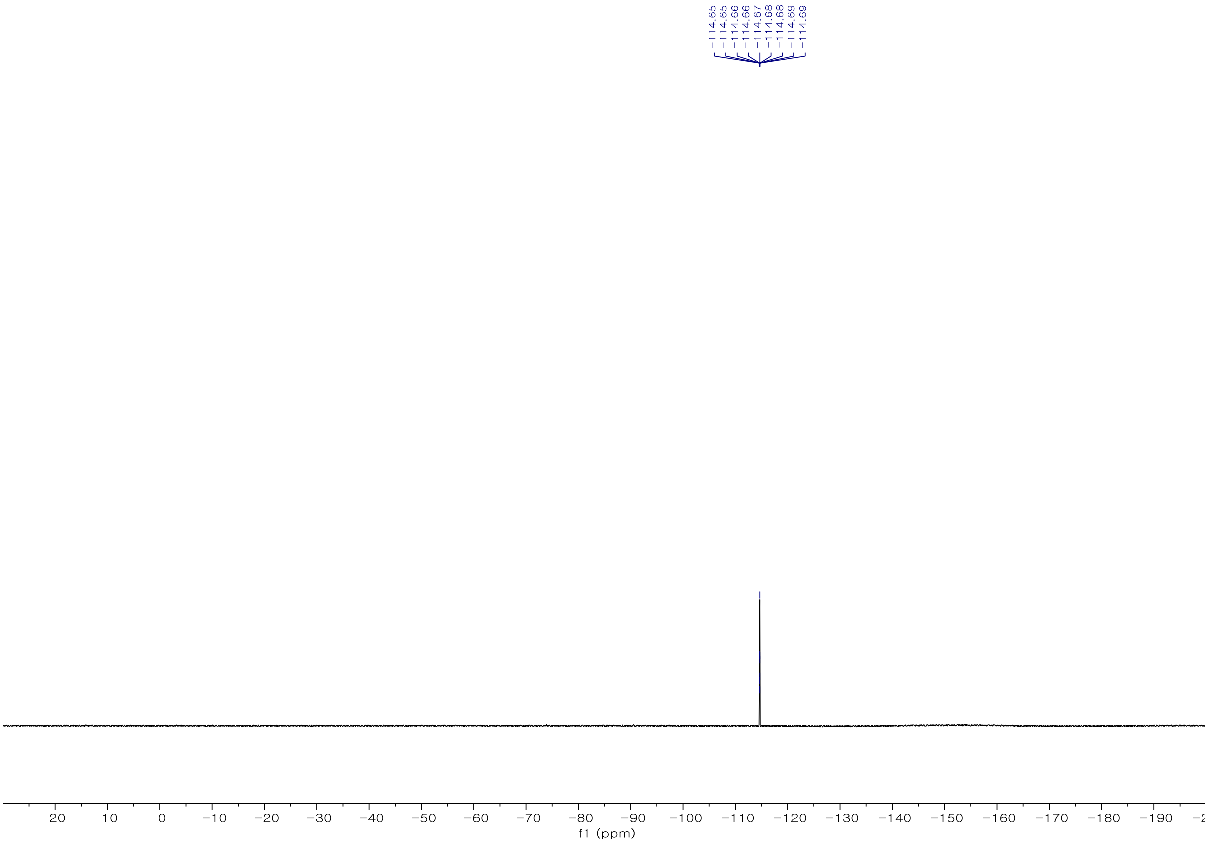
Appendix I

Spectral Copies of ^{1}H, ^{13}C and ^{19}F NMR of Compounds Obtained in this Study

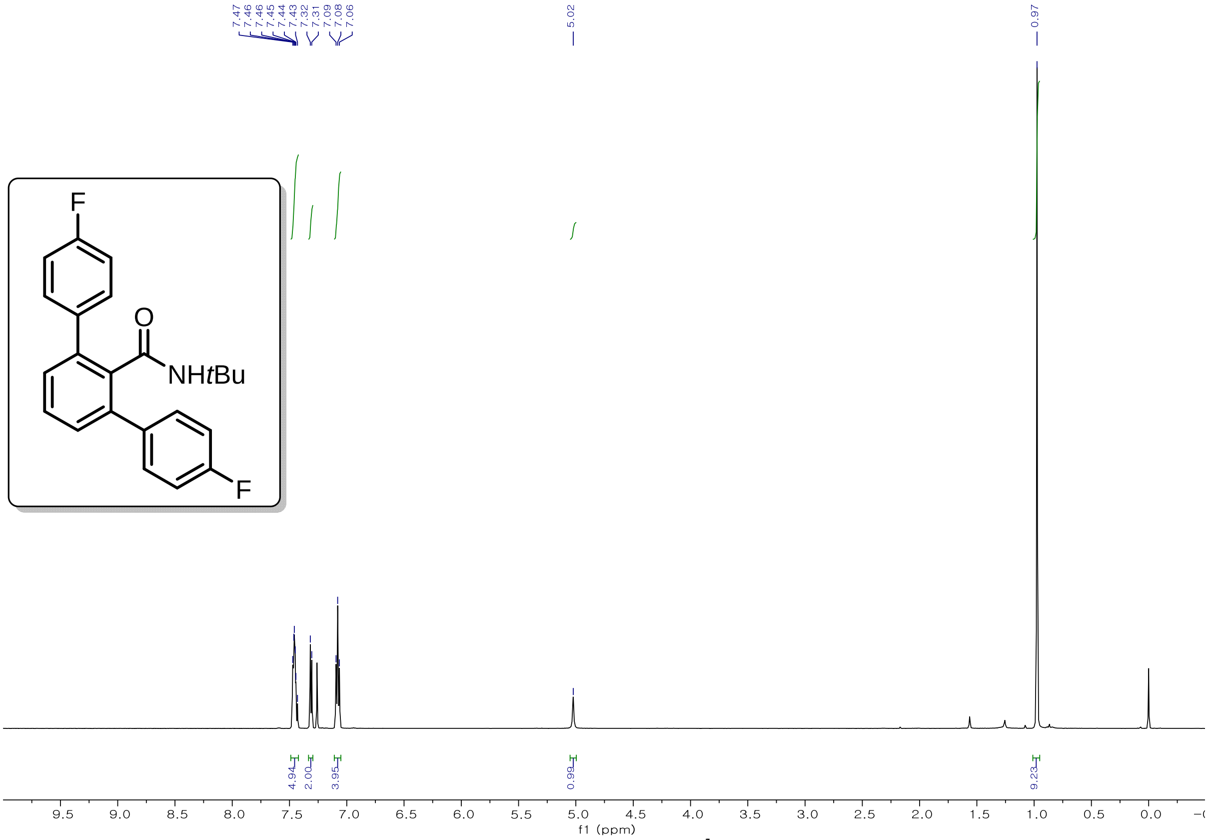
***N*-(*tert*-Butyl)-4'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3a**)

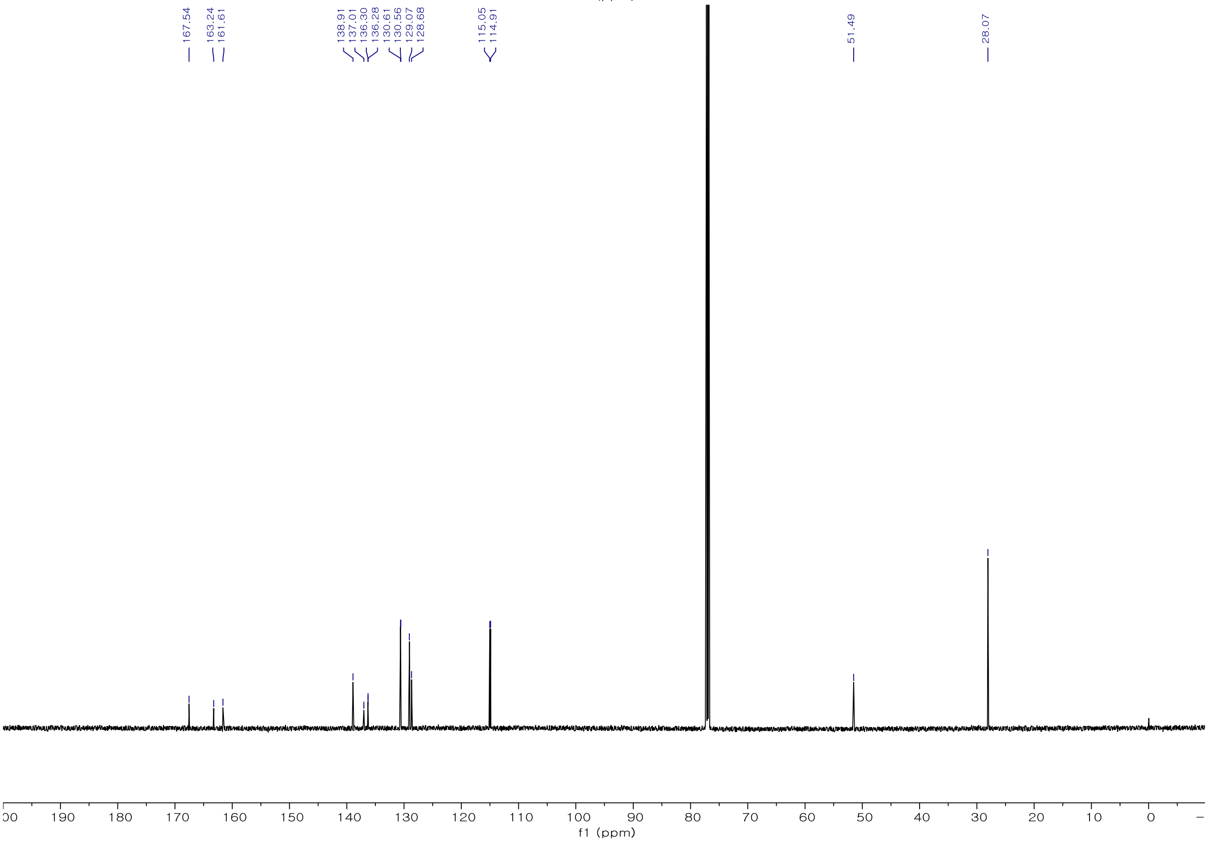


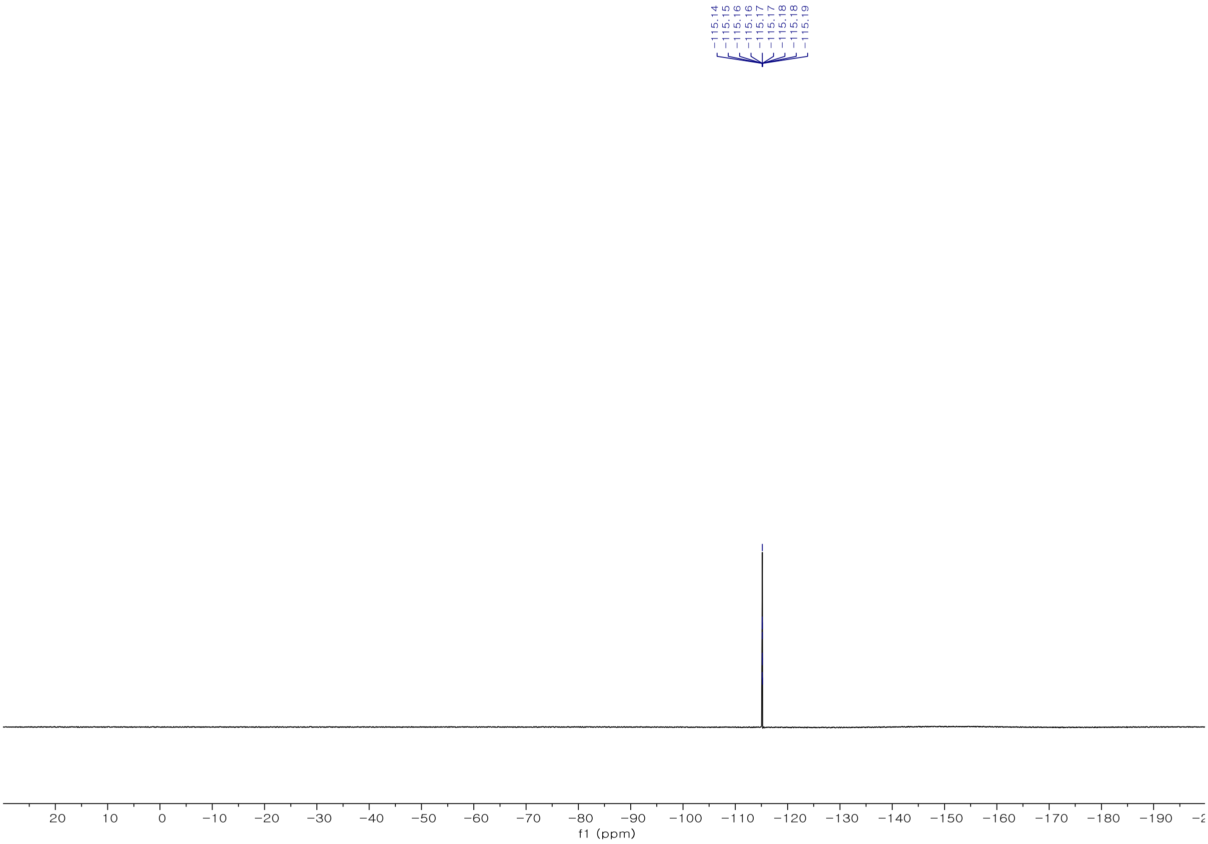



-114.65
-114.65
-114.66
-114.66
-114.67
-114.68
-114.68
-114.69
-114.69
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

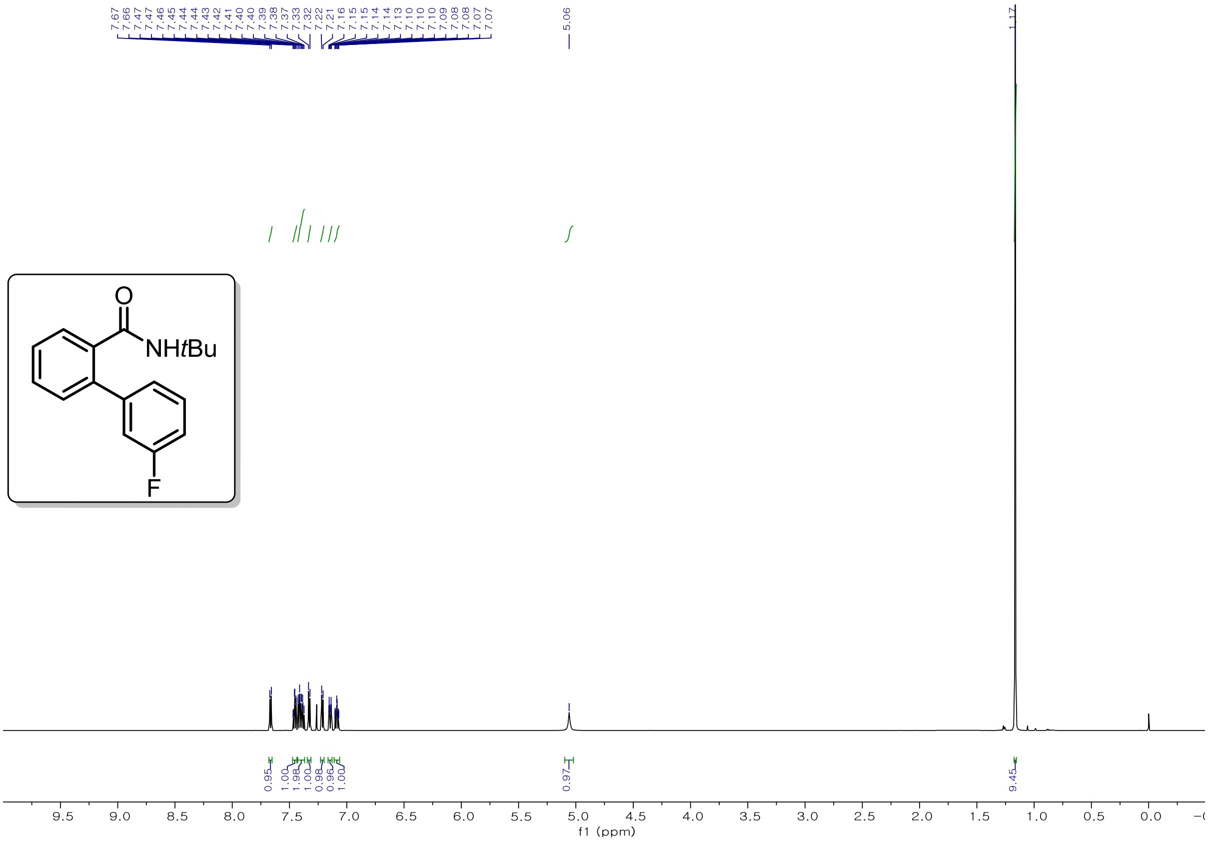
***N*-(*tert*-Butyl)-4,4''-difluoro-[1,1':3',1''-terphenyl]-2'-carboxamide** (Scheme 2, **3a'**)

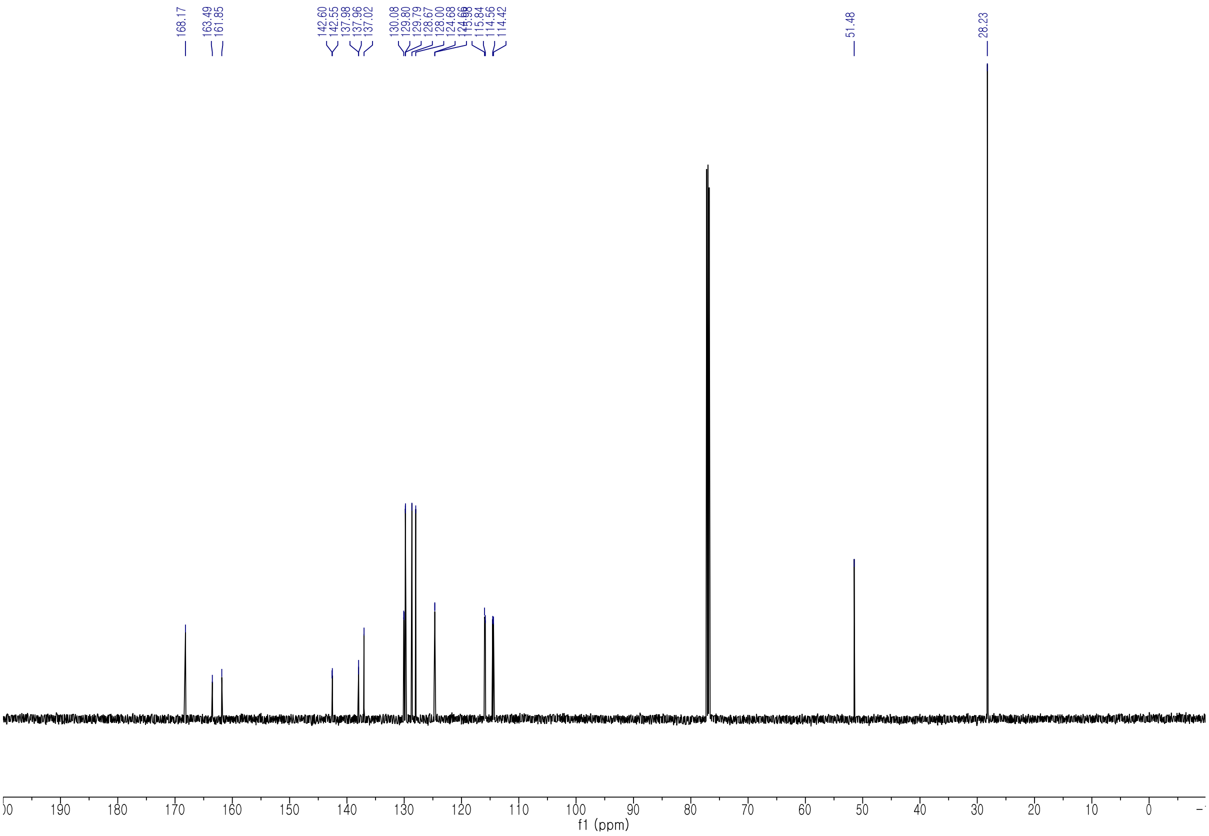


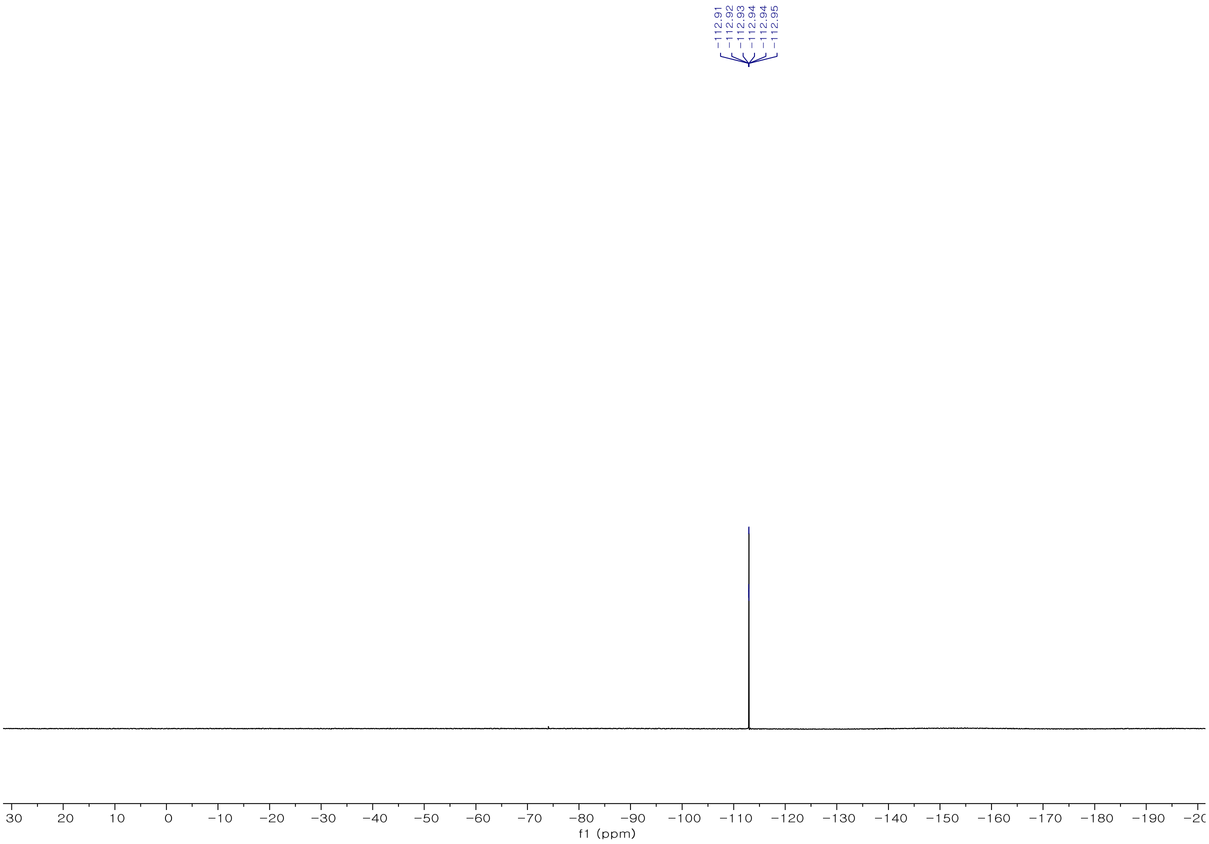



-115.14
-115.15
-115.16
-115.16
-115.17
-115.17
-115.18
-115.18
-115.19
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

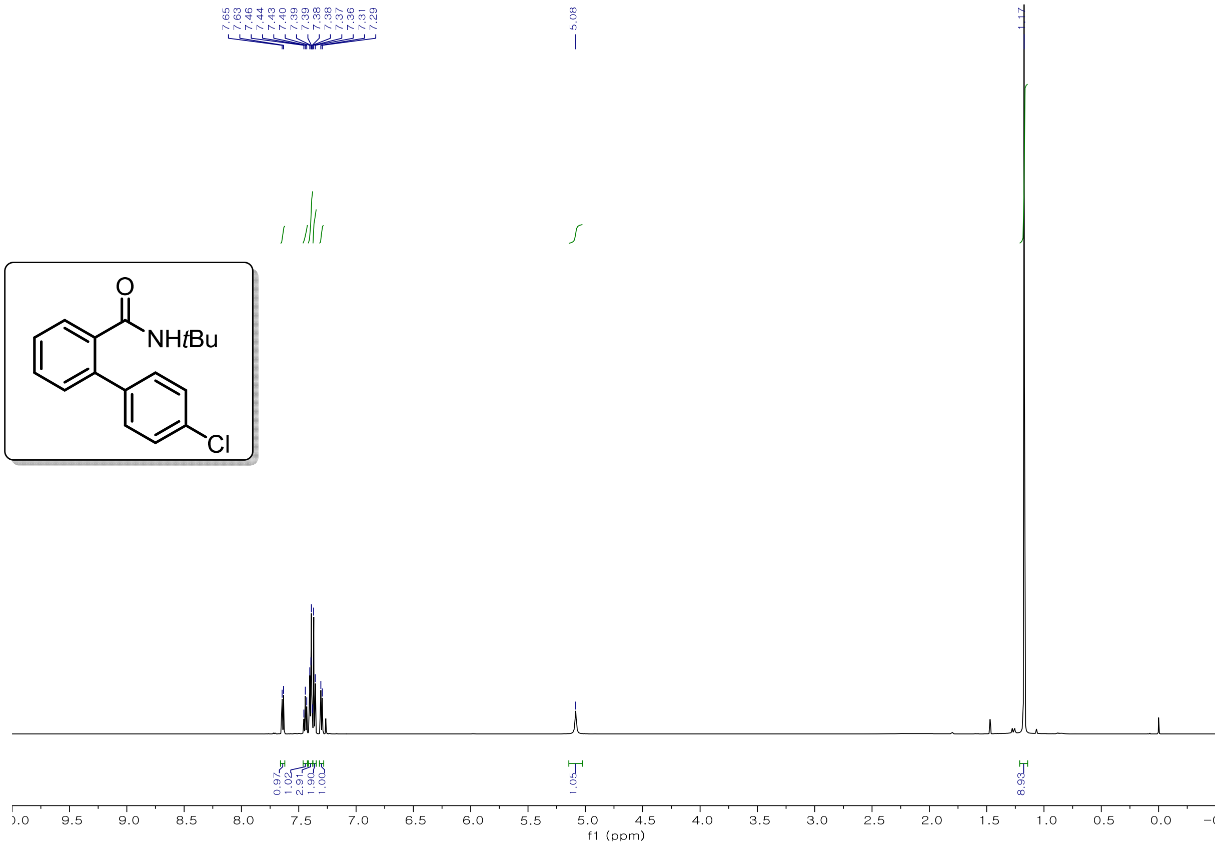
***N*-(*tert*-Butyl)-3'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3b**)

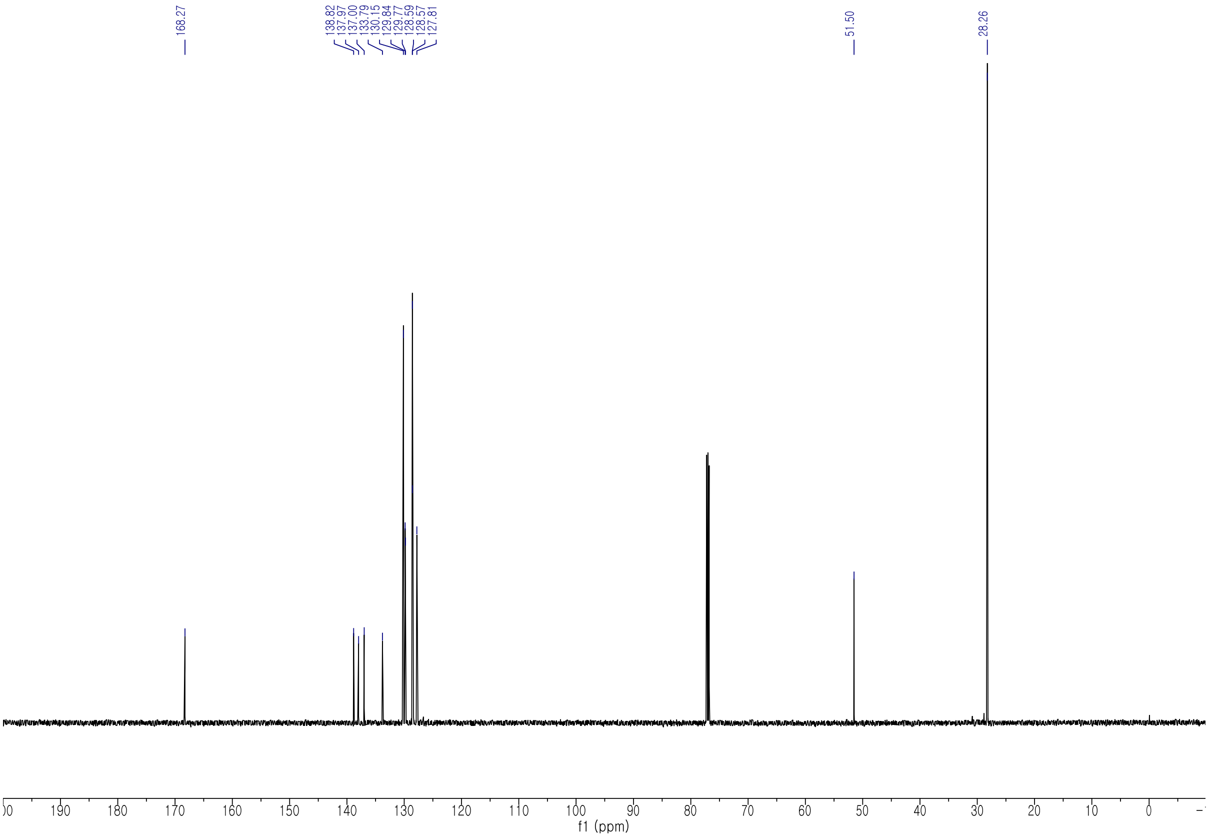




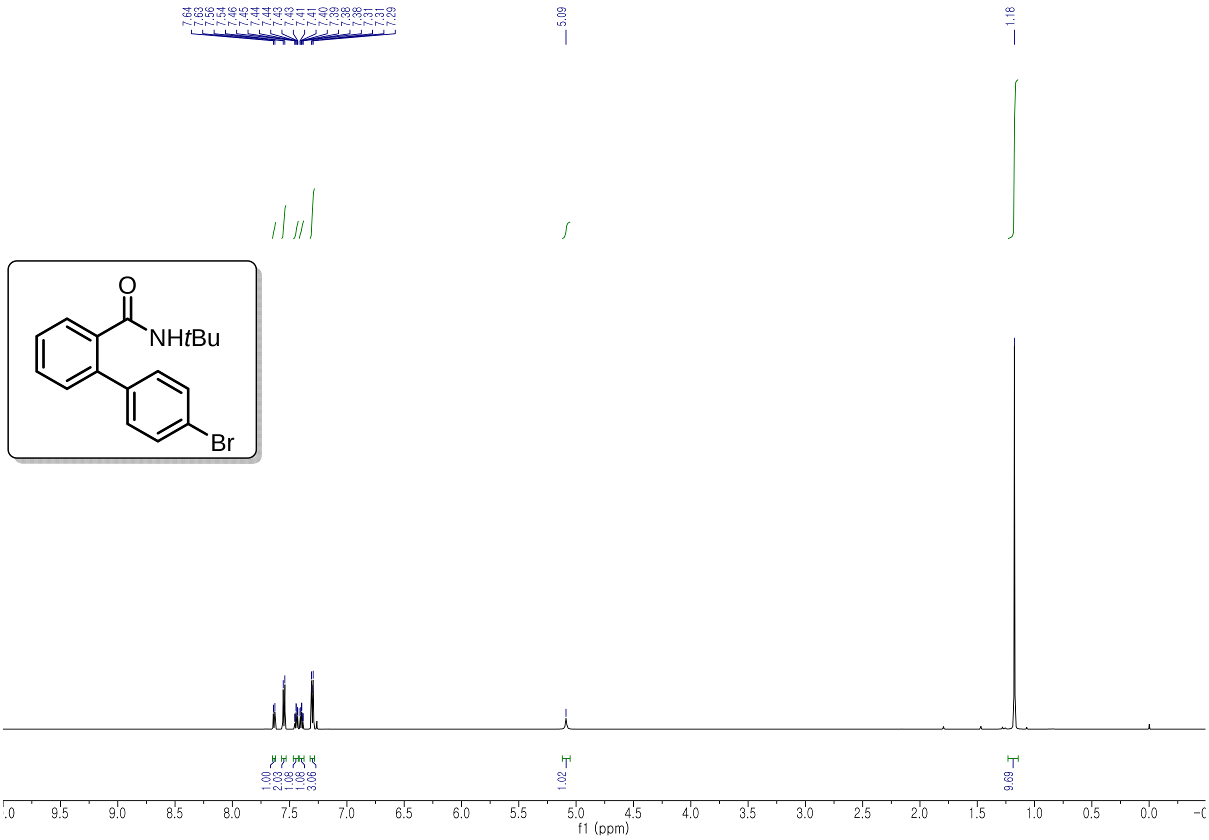

-112.91
-112.92
-112.93
-112.94
-112.94
-112.95
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

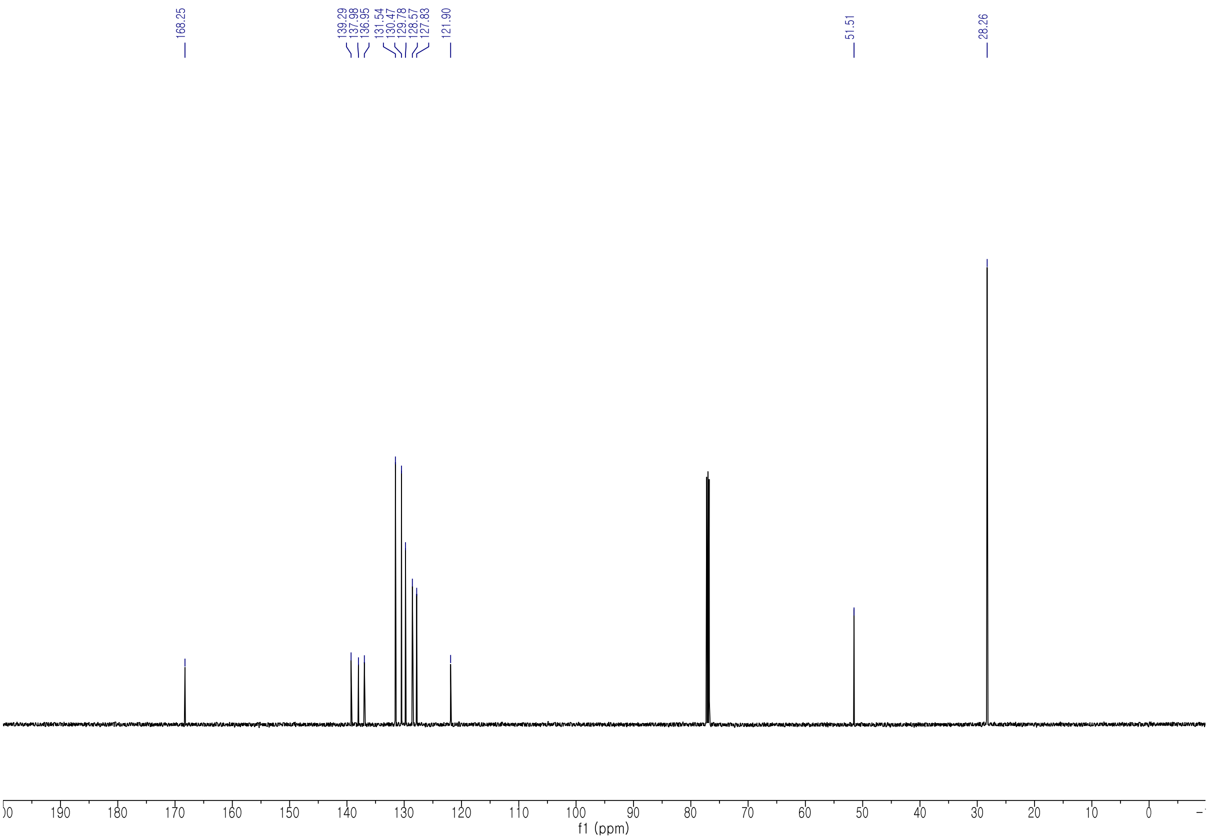
***N*-(*tert*-Butyl)-4'-chloro-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3c**)



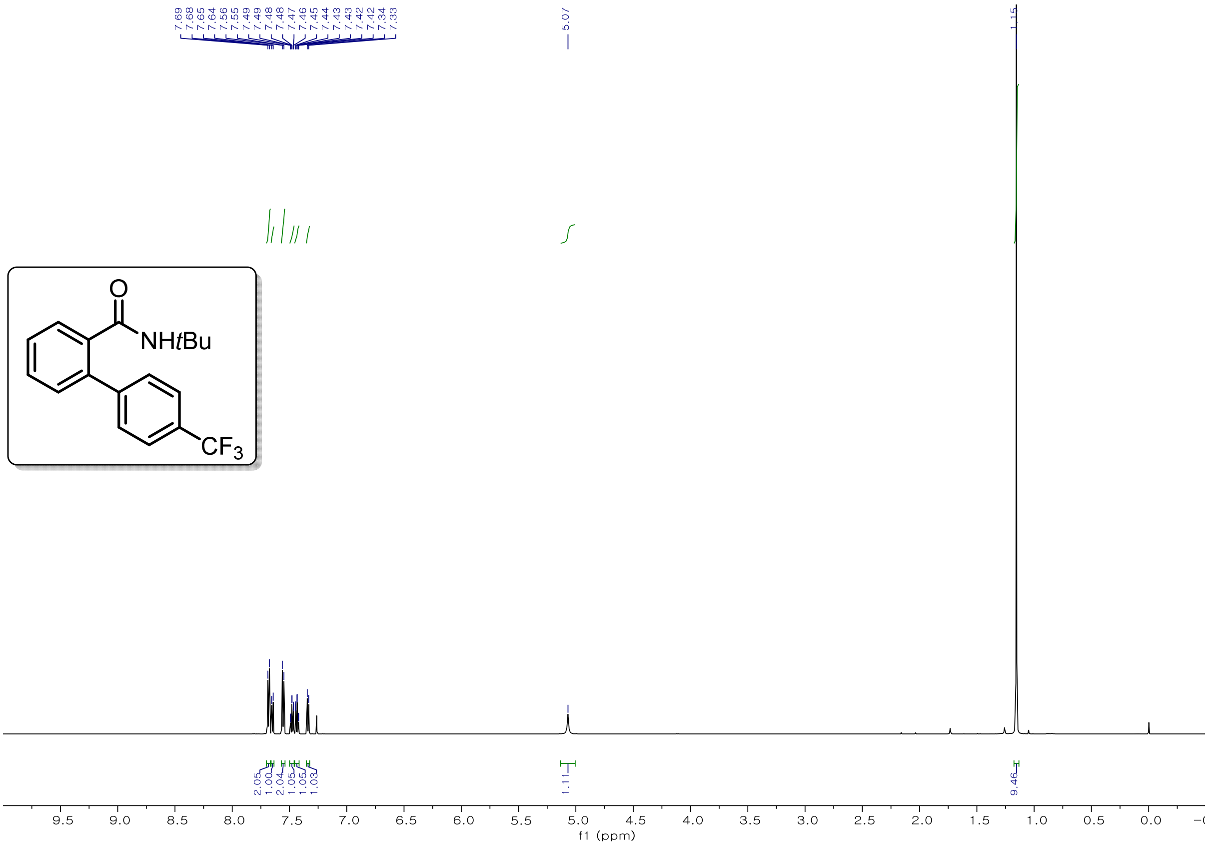


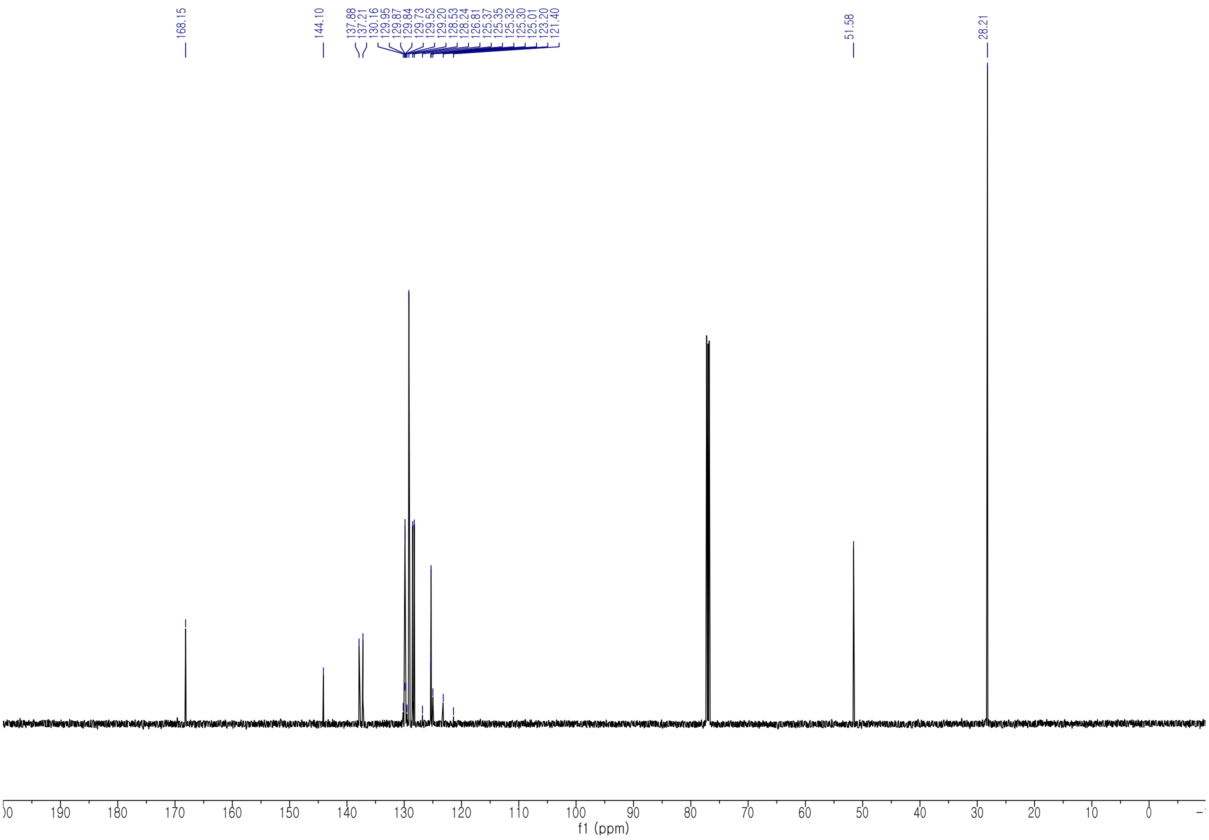
***N*-(*tert*-Butyl)-4'-bromo-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3d**)

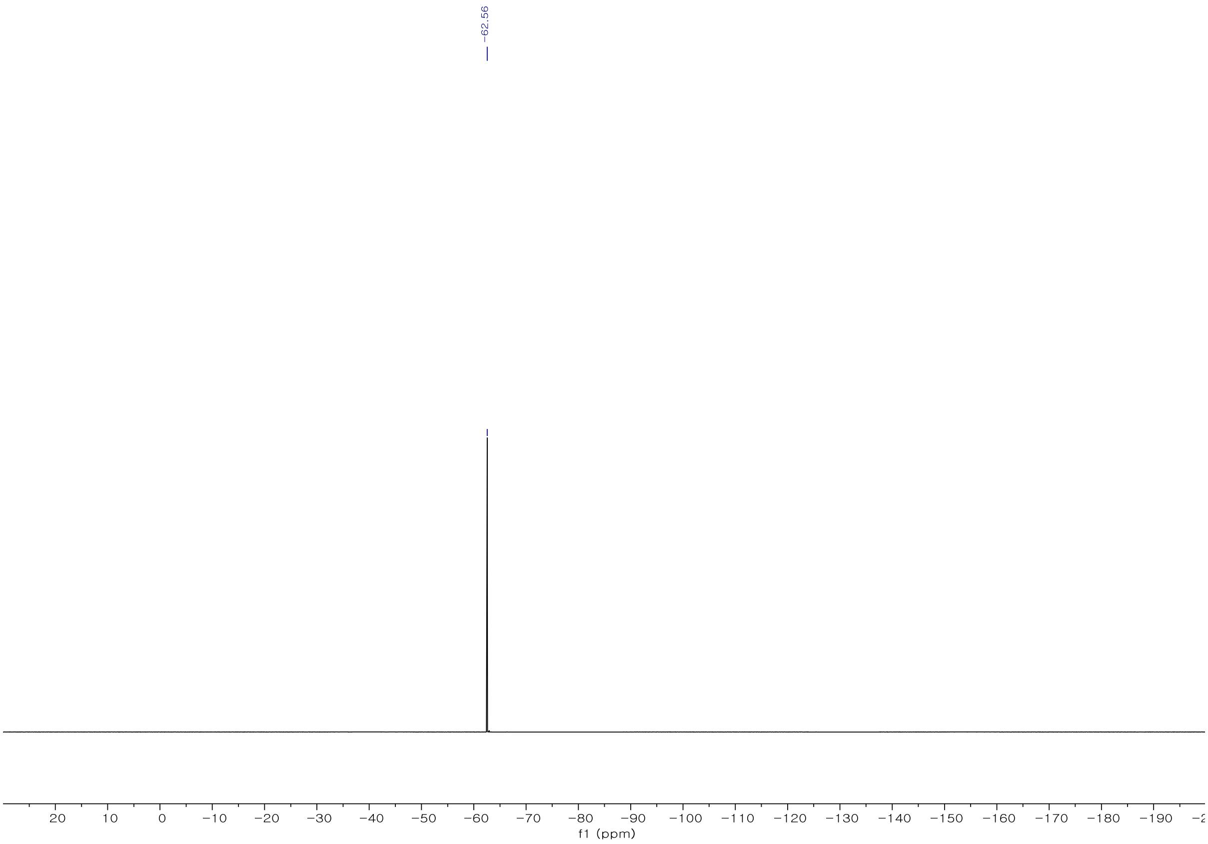




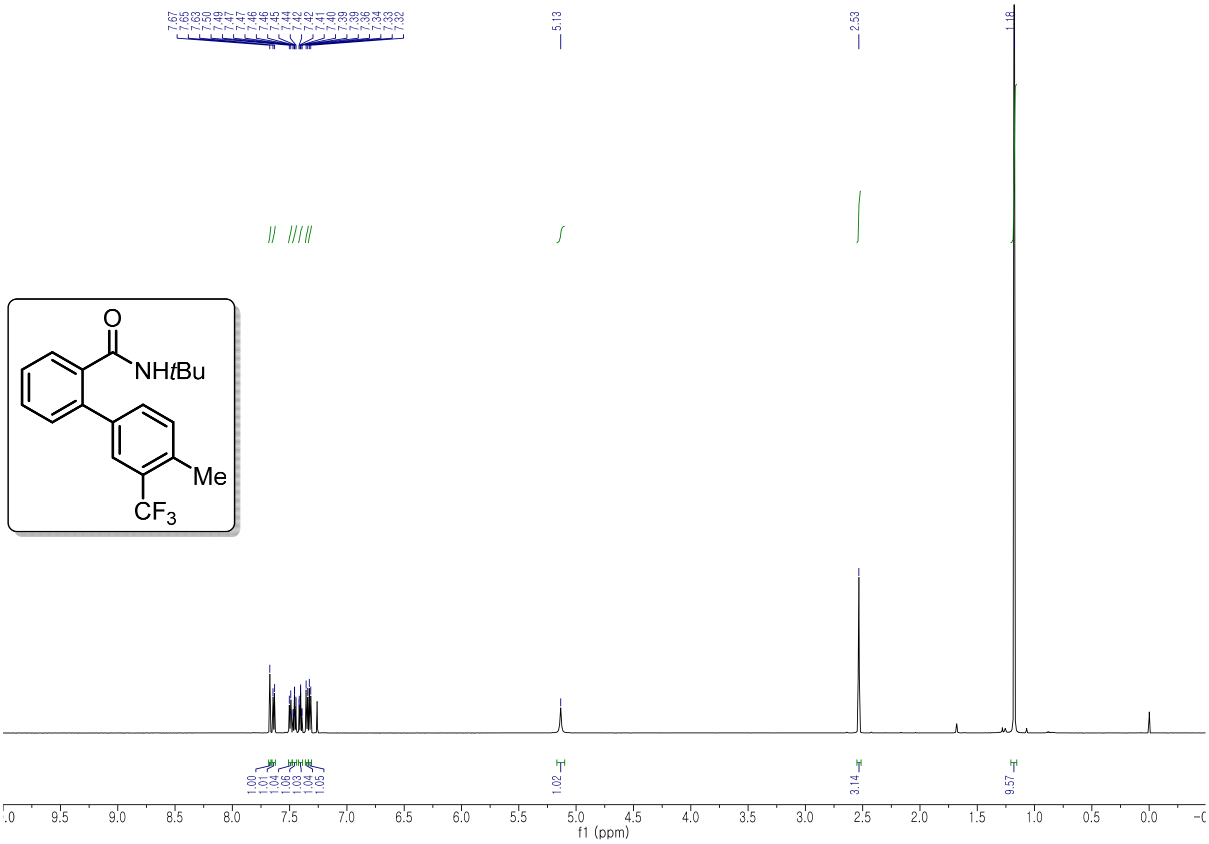
***N*-(*tert*-Butyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3e**)

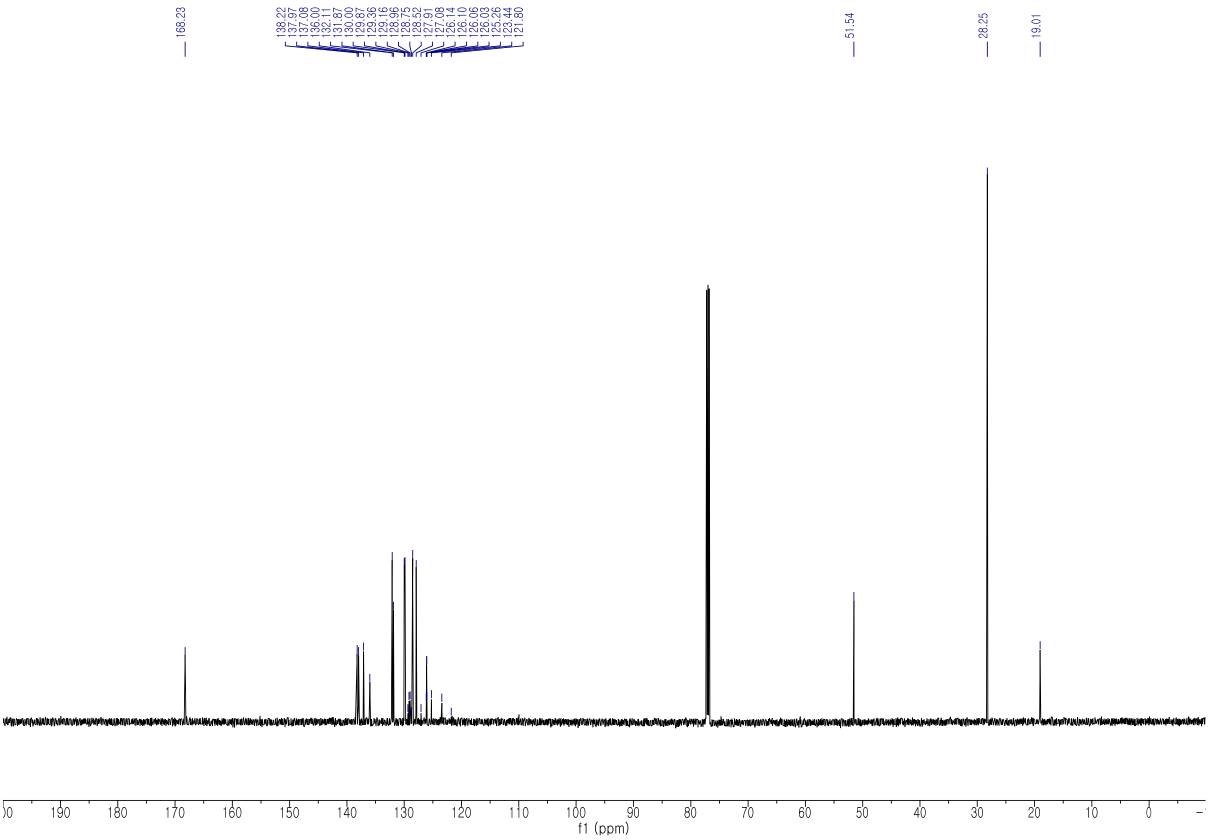


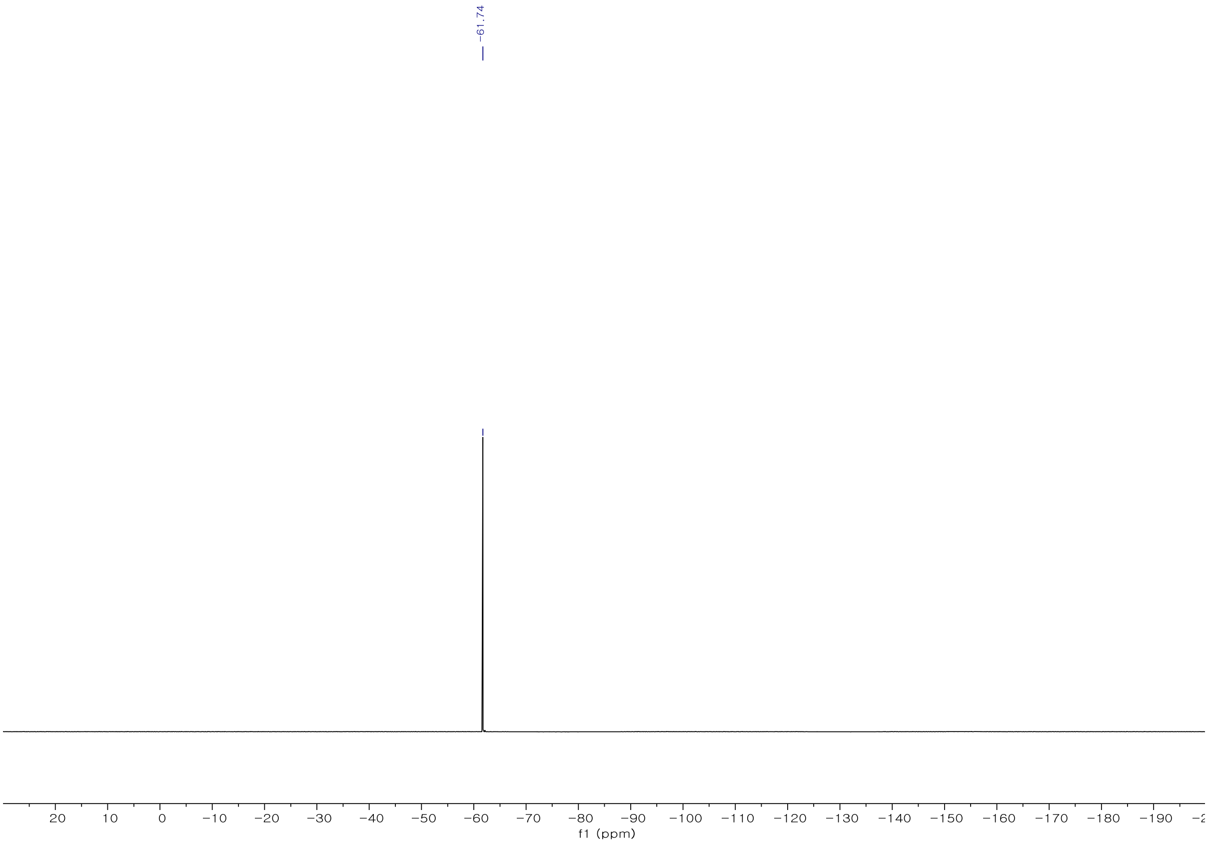



-62.56
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

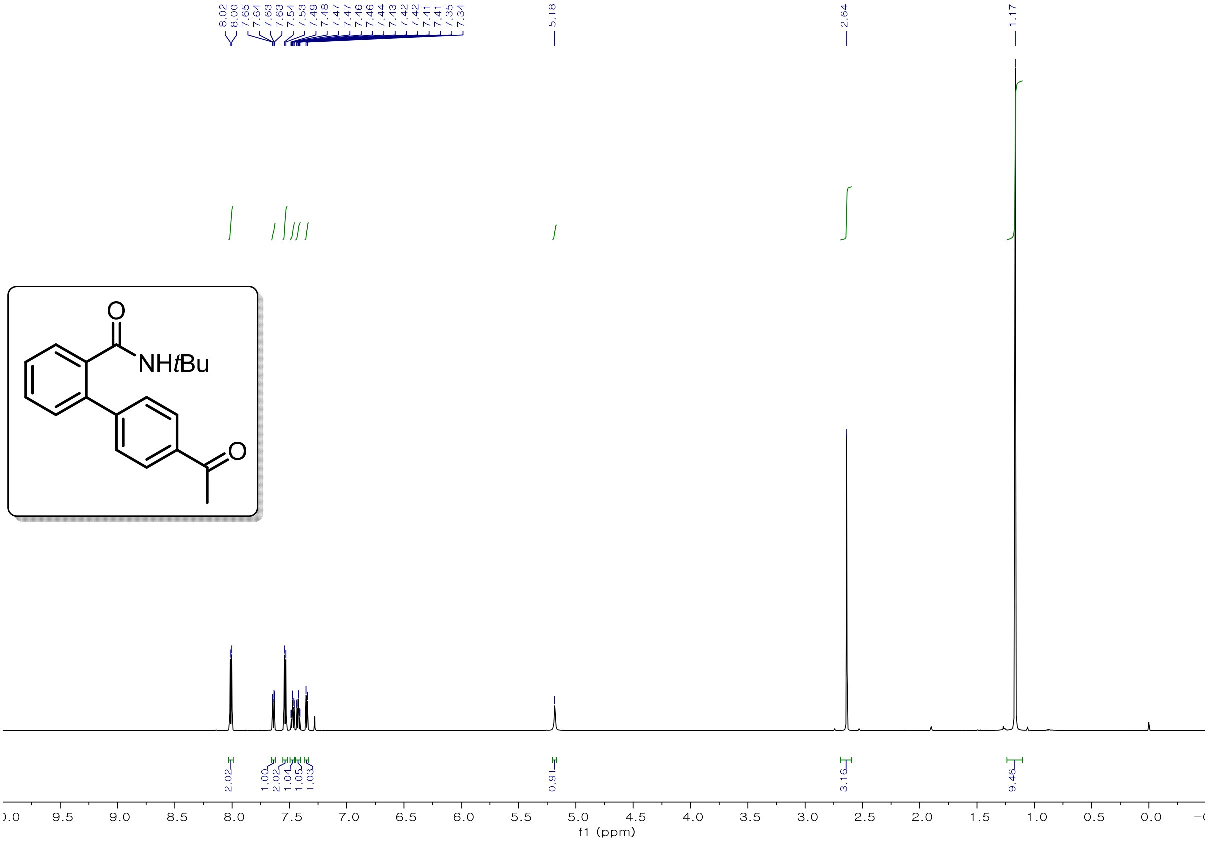
***N*-(*tert*-Butyl)- 4'-methyl-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3f**)

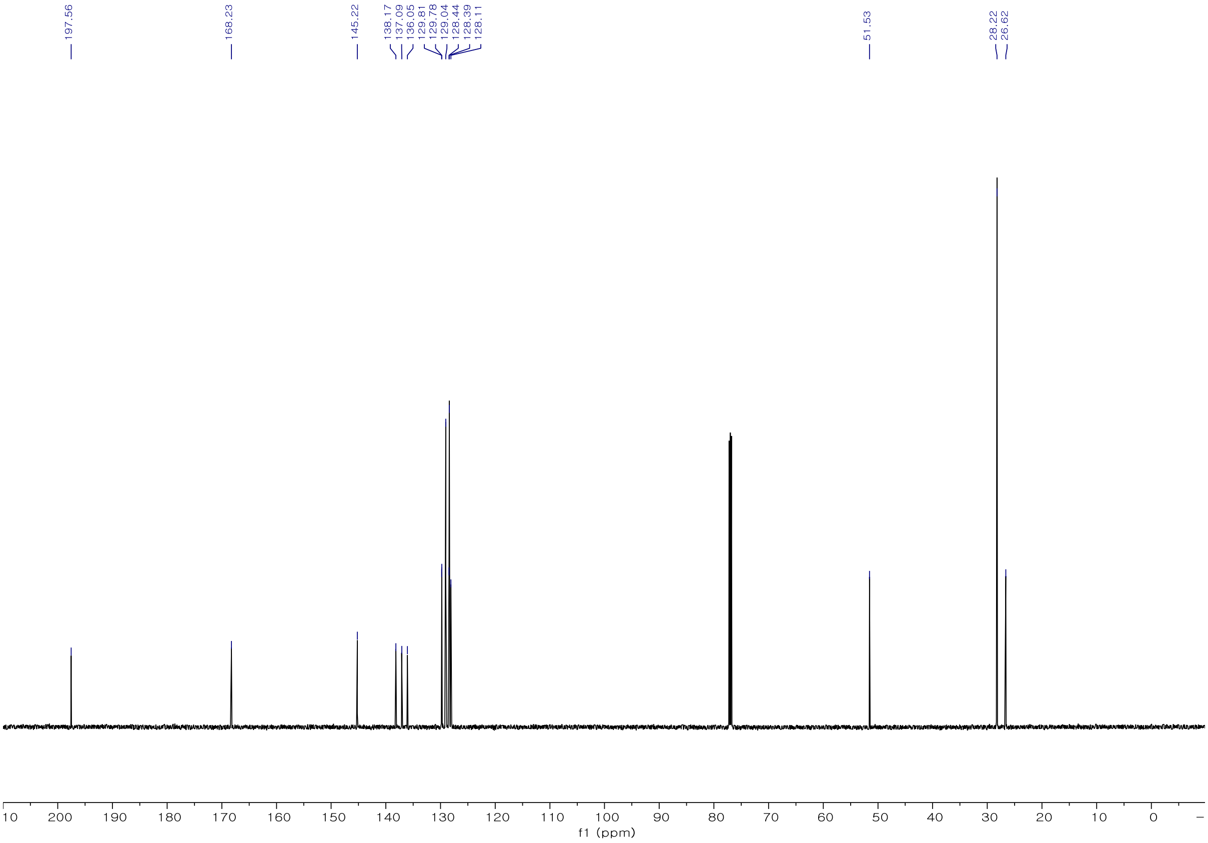




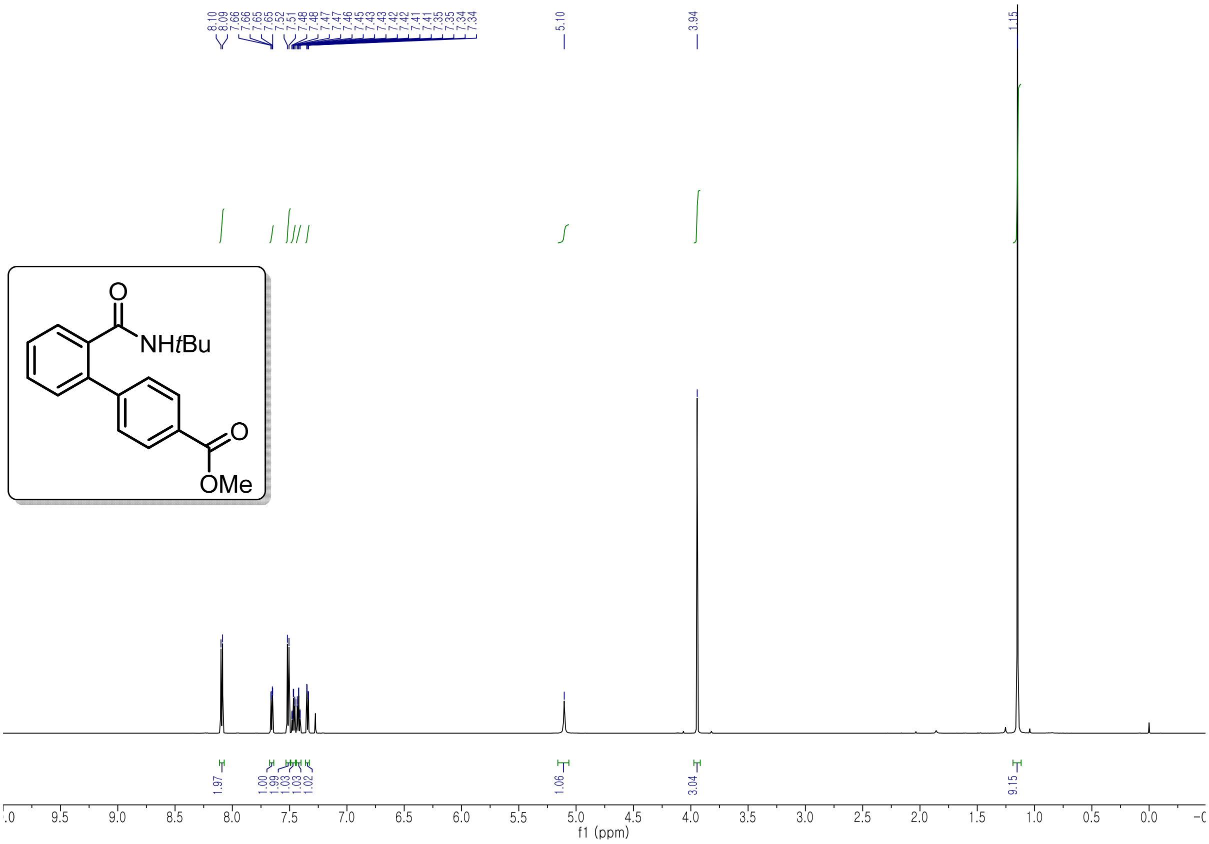

-61.74
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

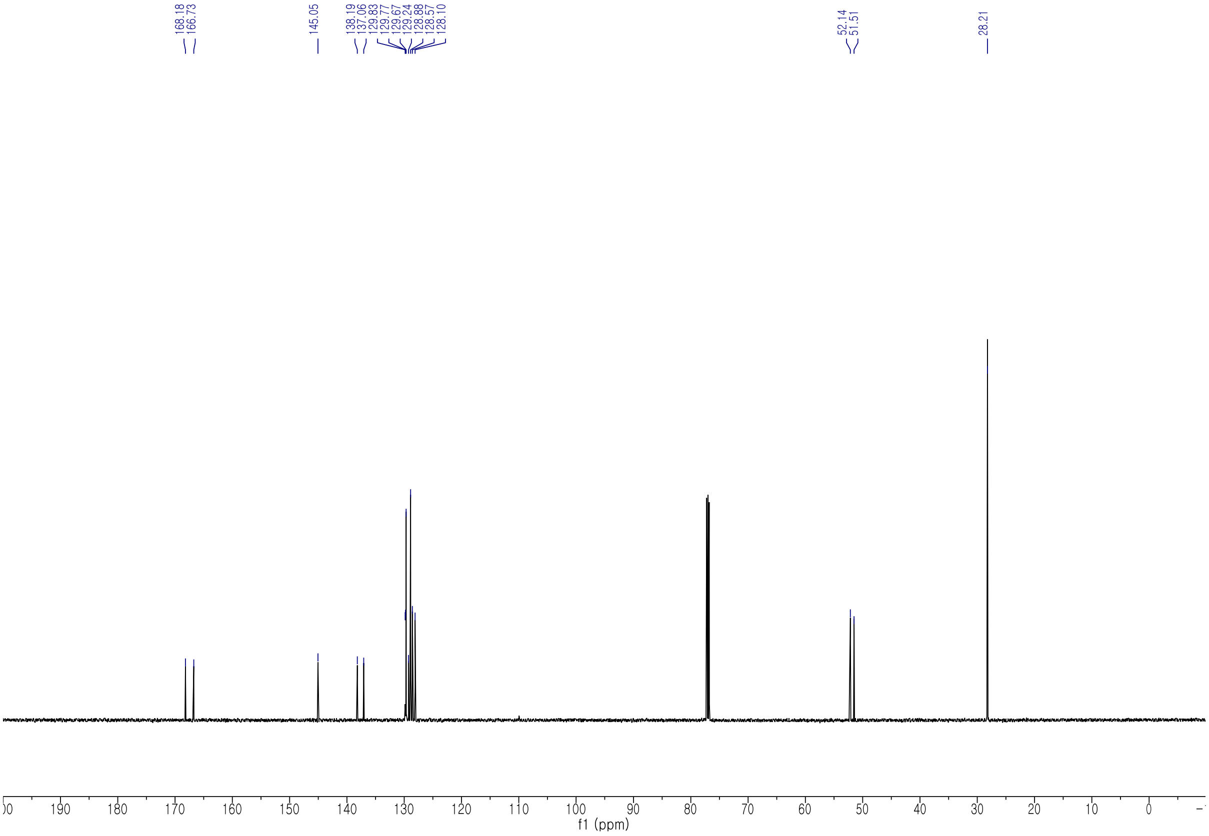
***N*-(*tert*-Butyl)-4'-acetyl-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3g**)



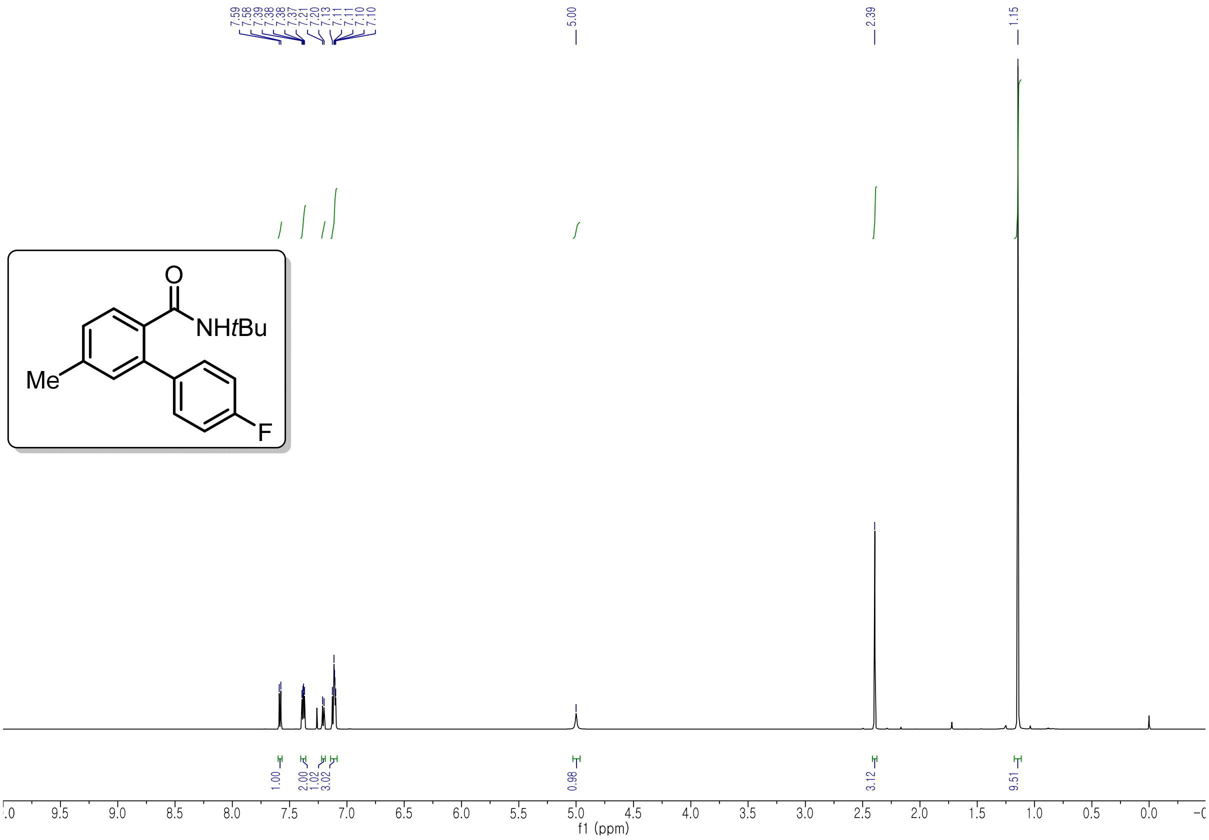


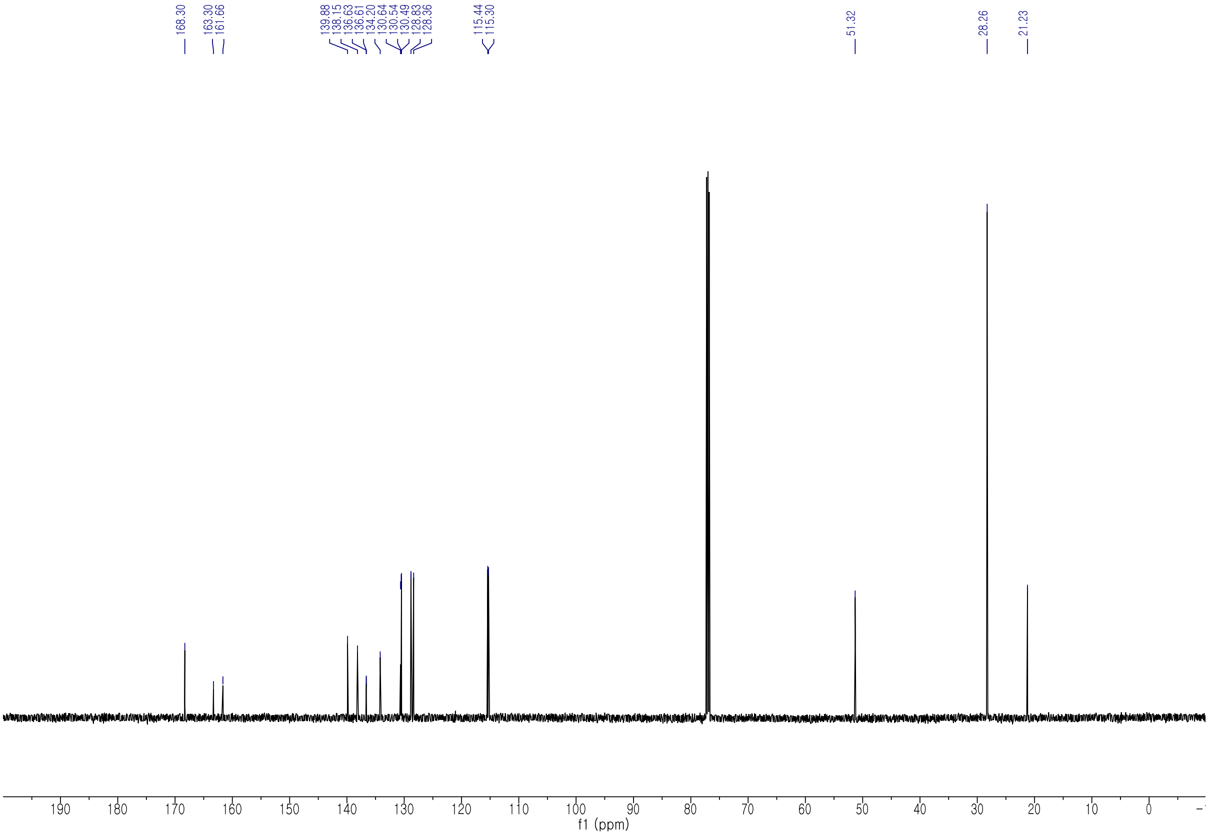
***N*-(*tert*-Butyl)-4'-methoxycarbonyl-[1,1'-biphenyl]-2-carboxamide** (Table 2, **3h**)

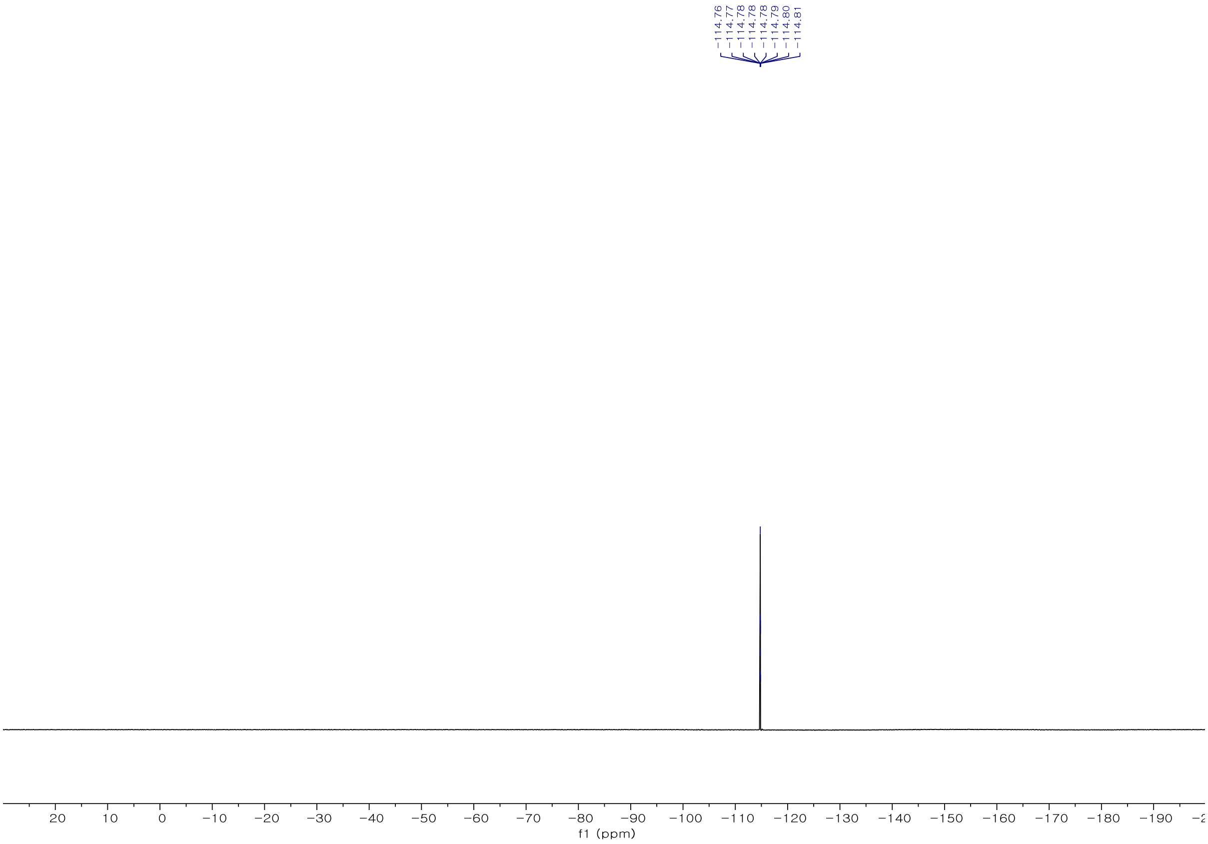




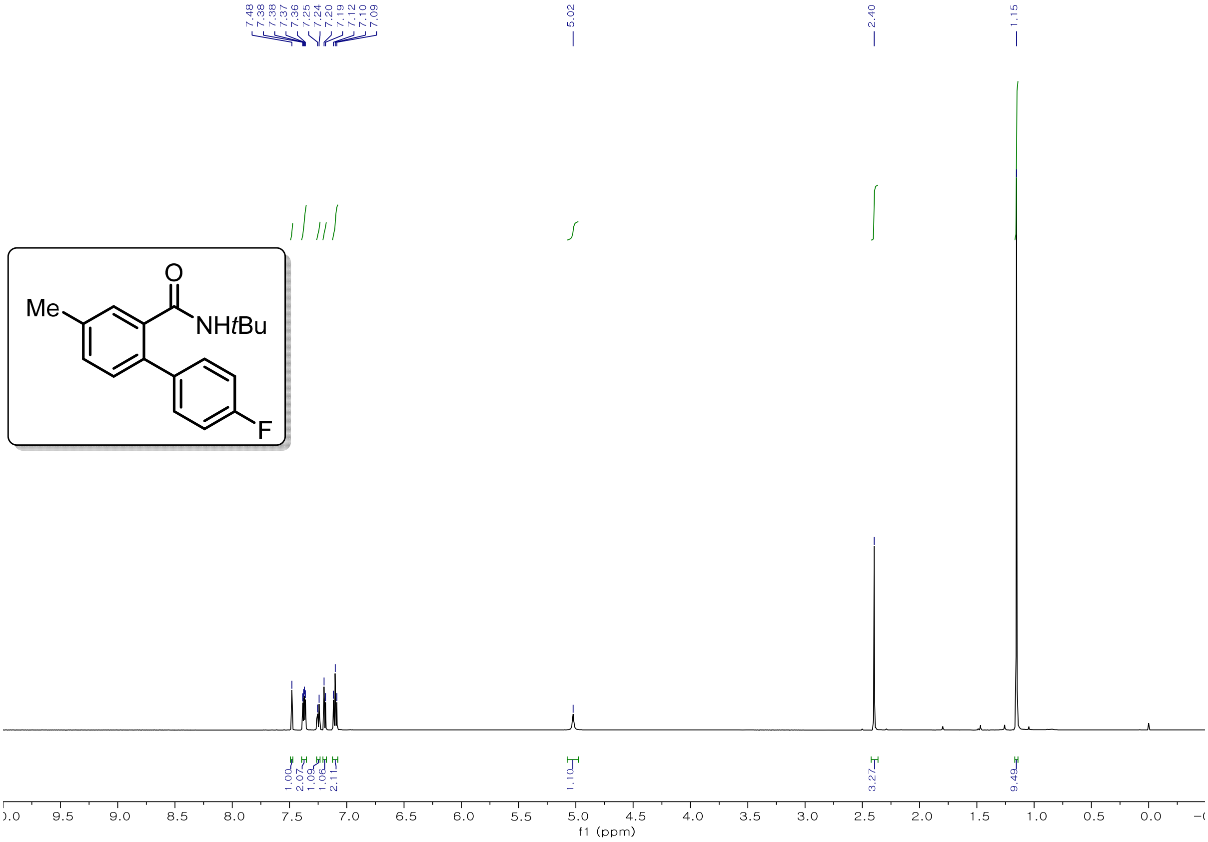
***N*-(*tert*-Butyl)-4'-fluoro-5-methyl-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3i**)

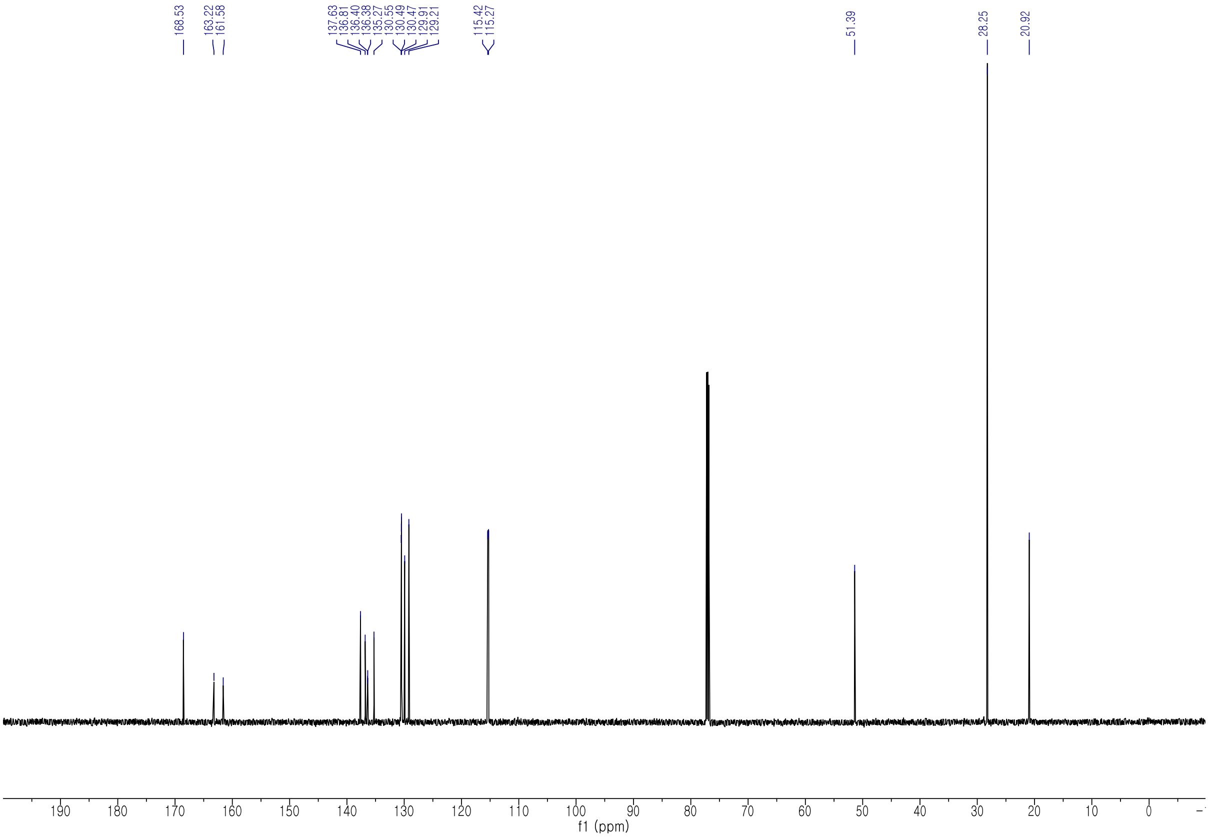


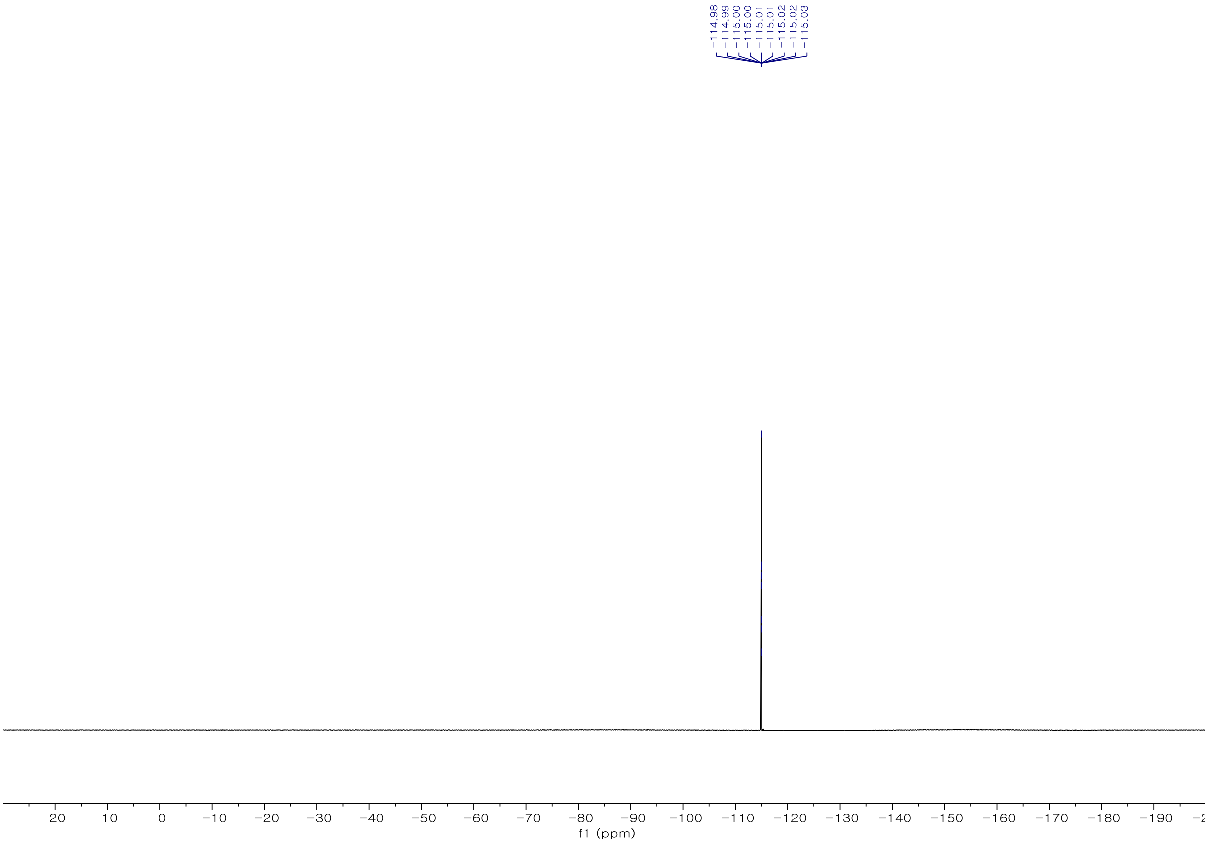



-114.76
-114.77
-114.78
-114.78
-114.79
-114.80
-114.81
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

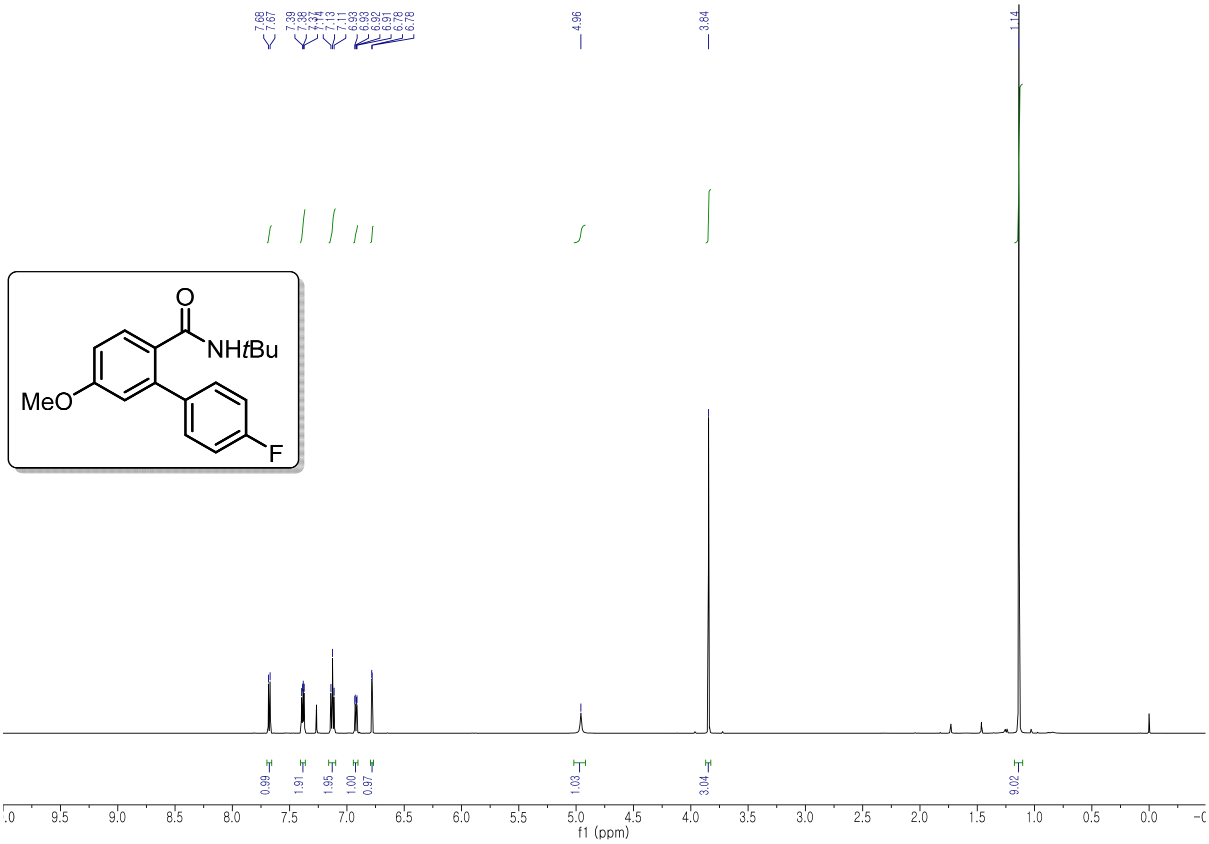
***N*-(*tert*-Butyl)-4'-fluoro-4-methyl-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3j**)

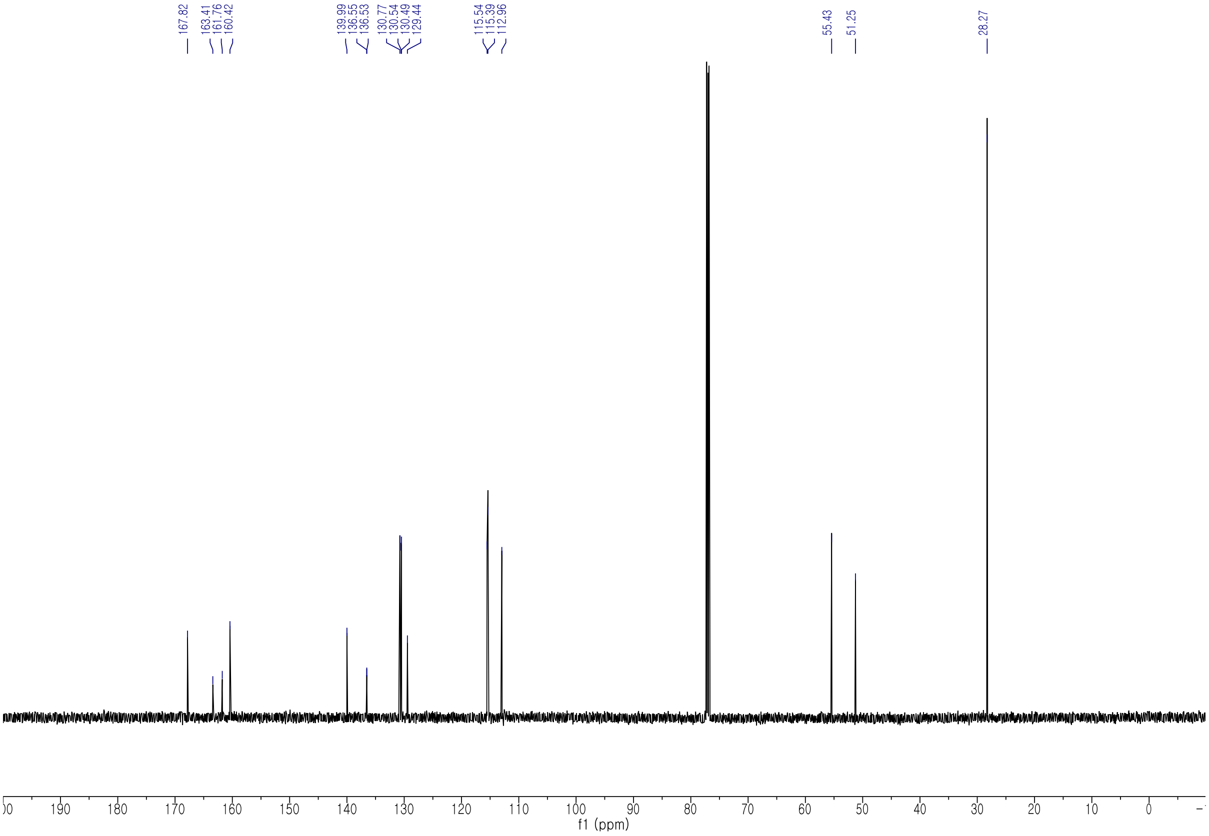


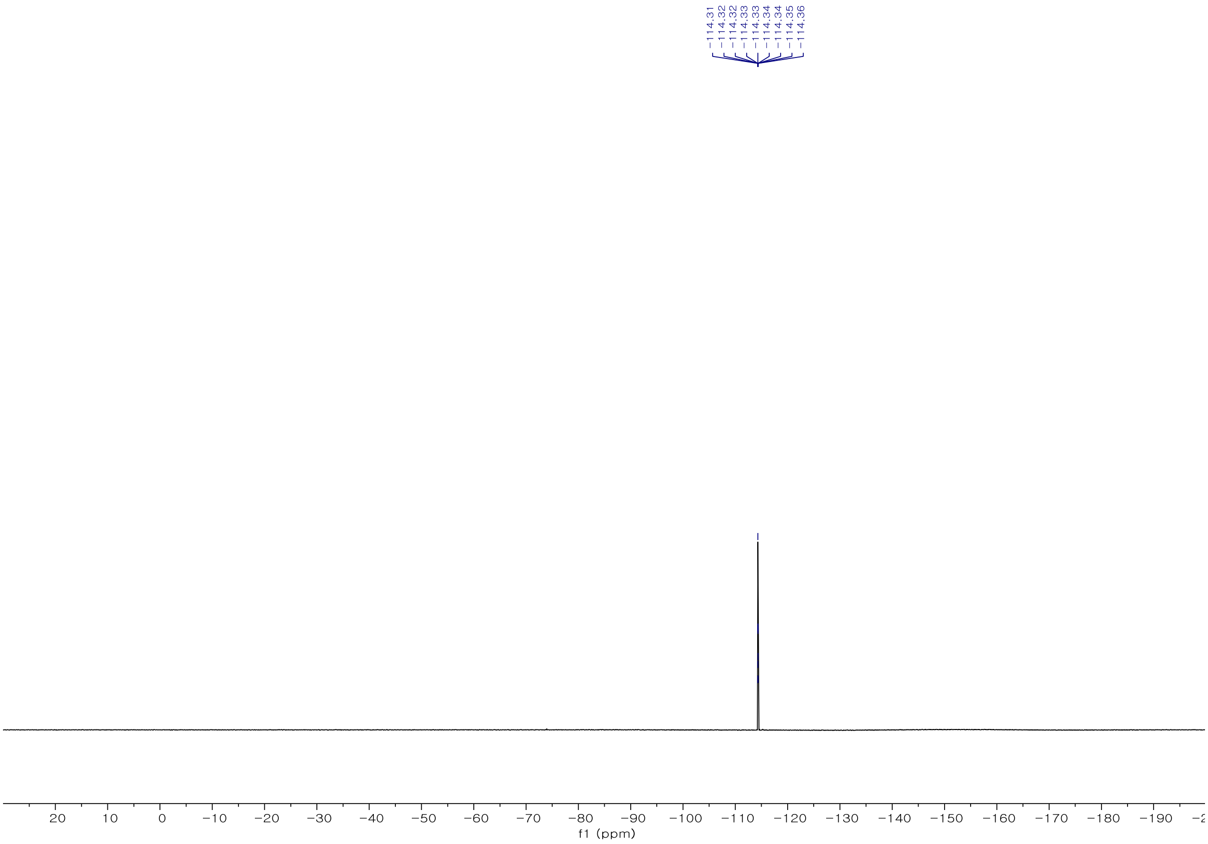



-114.98
-114.99
-115.00
-115.00
-115.01
-115.01
-115.02
-115.02
-115.03
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

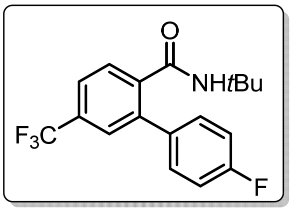
***N*-(*tert*-Butyl)-4'-fluoro-5-methoxy-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3k**)

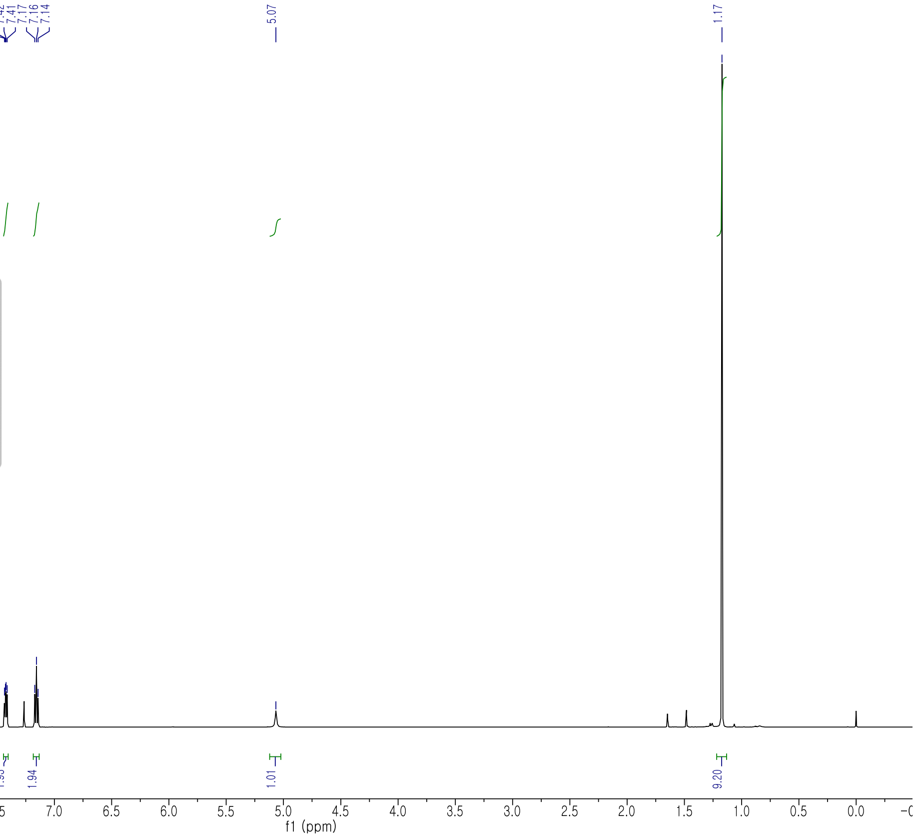


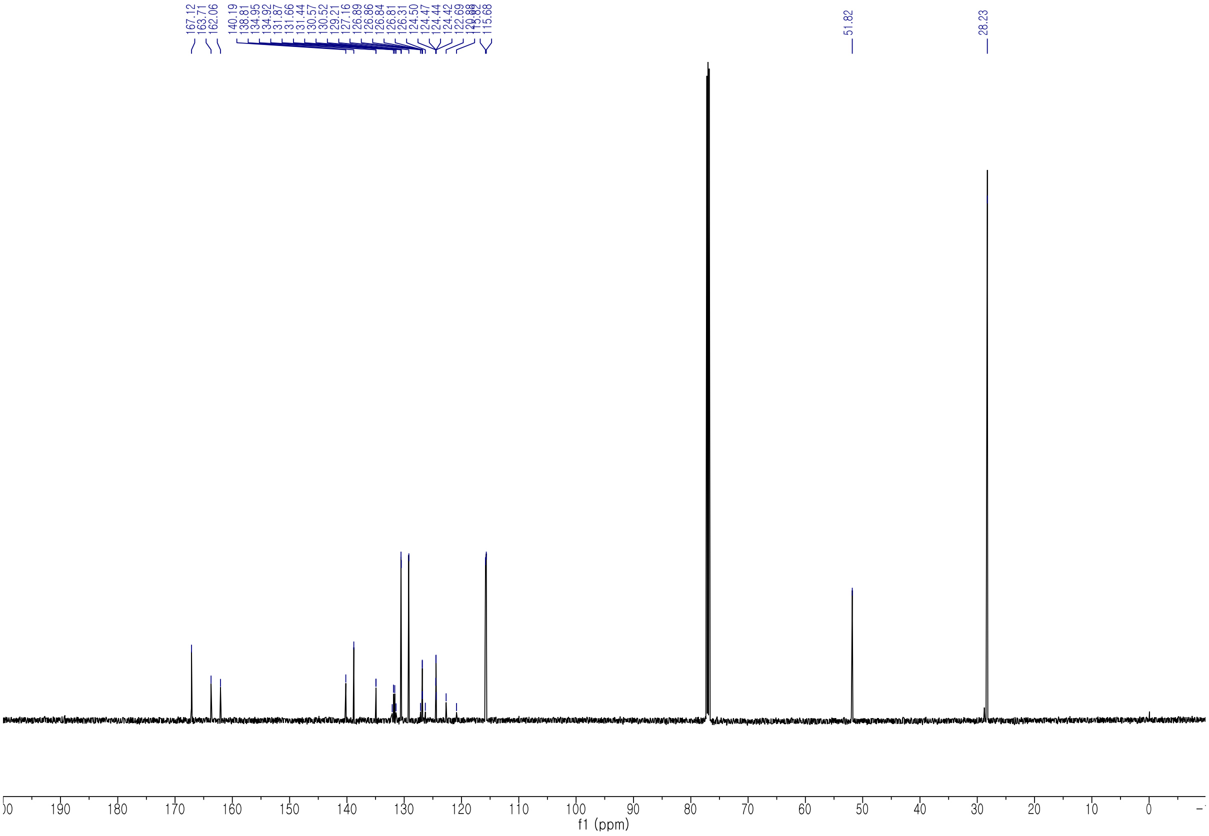


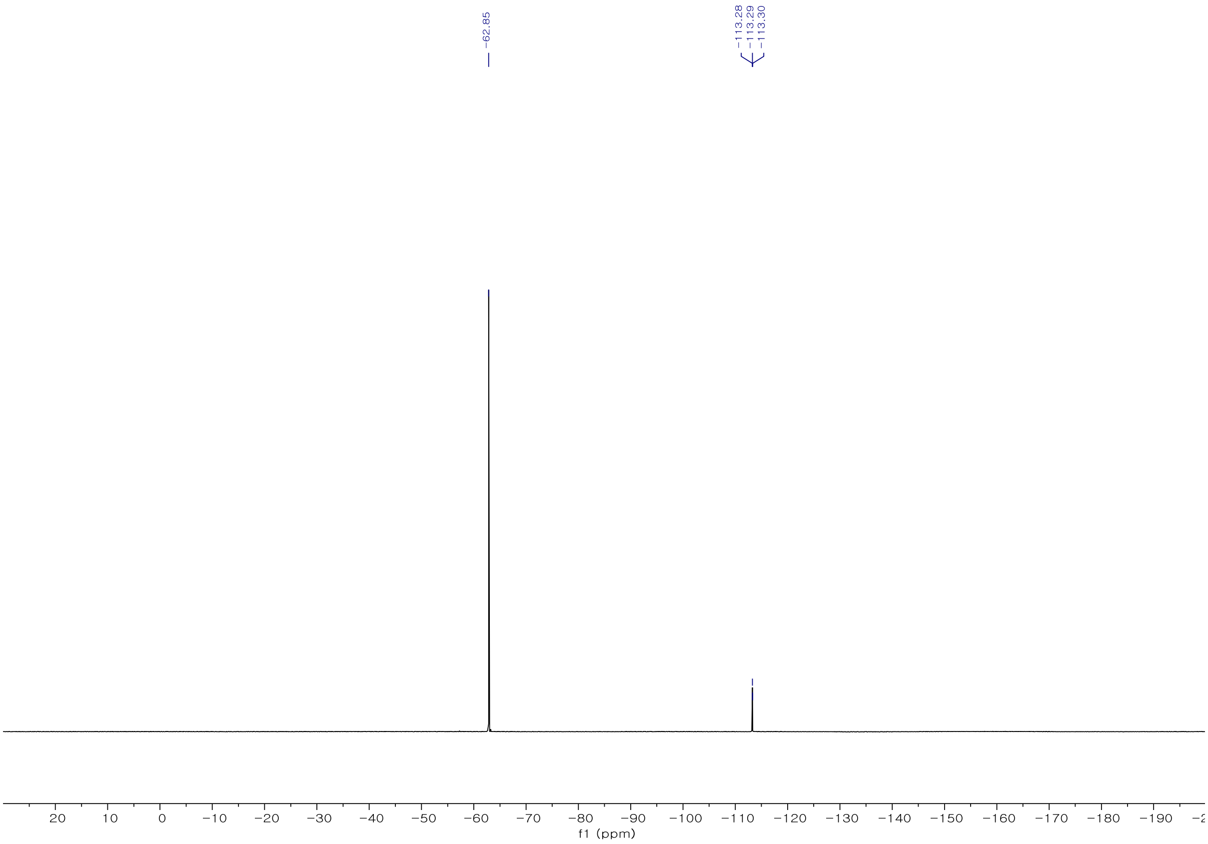

-114.31
-114.32
-114.32
-114.33
-114.33
-114.34
-114.34
-114.35
-114.36
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

N-(tert-Butyl)-4'-fluoro-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (Table 3, **3l**)



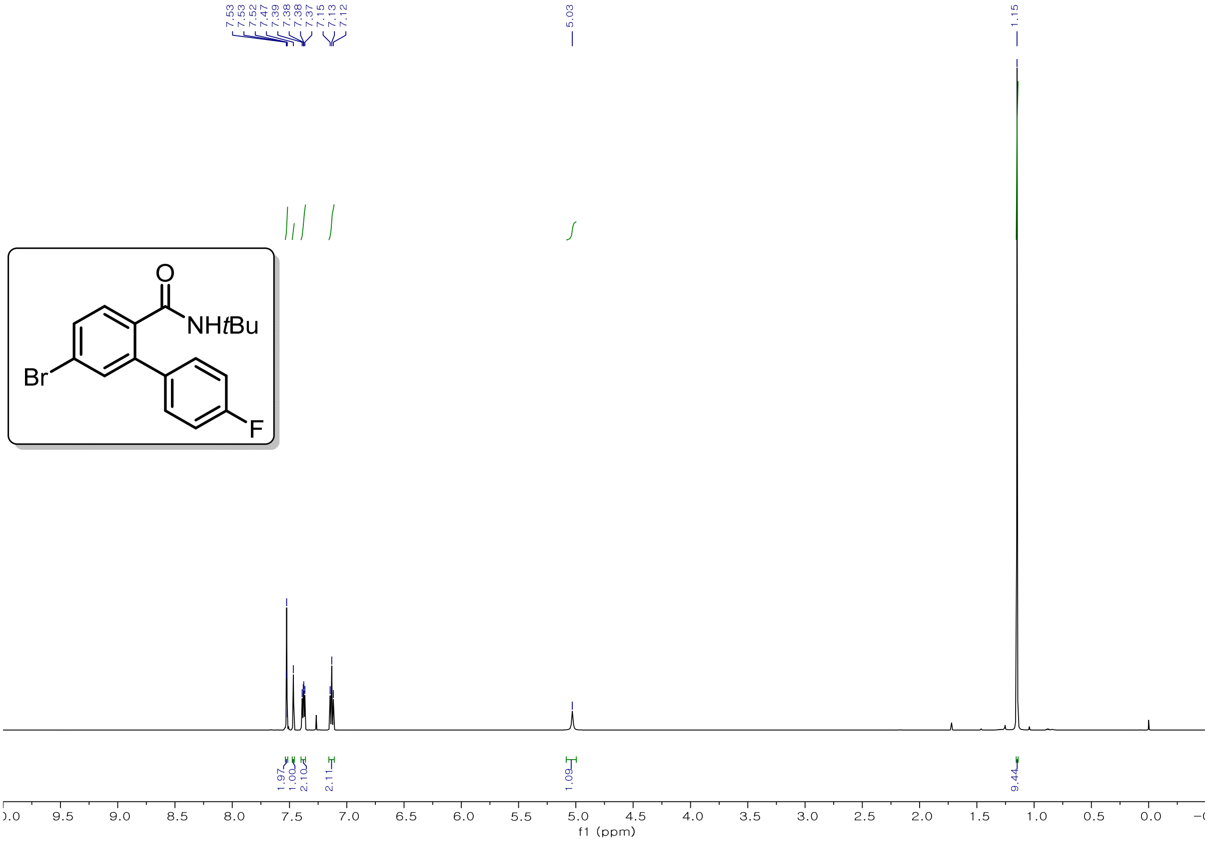


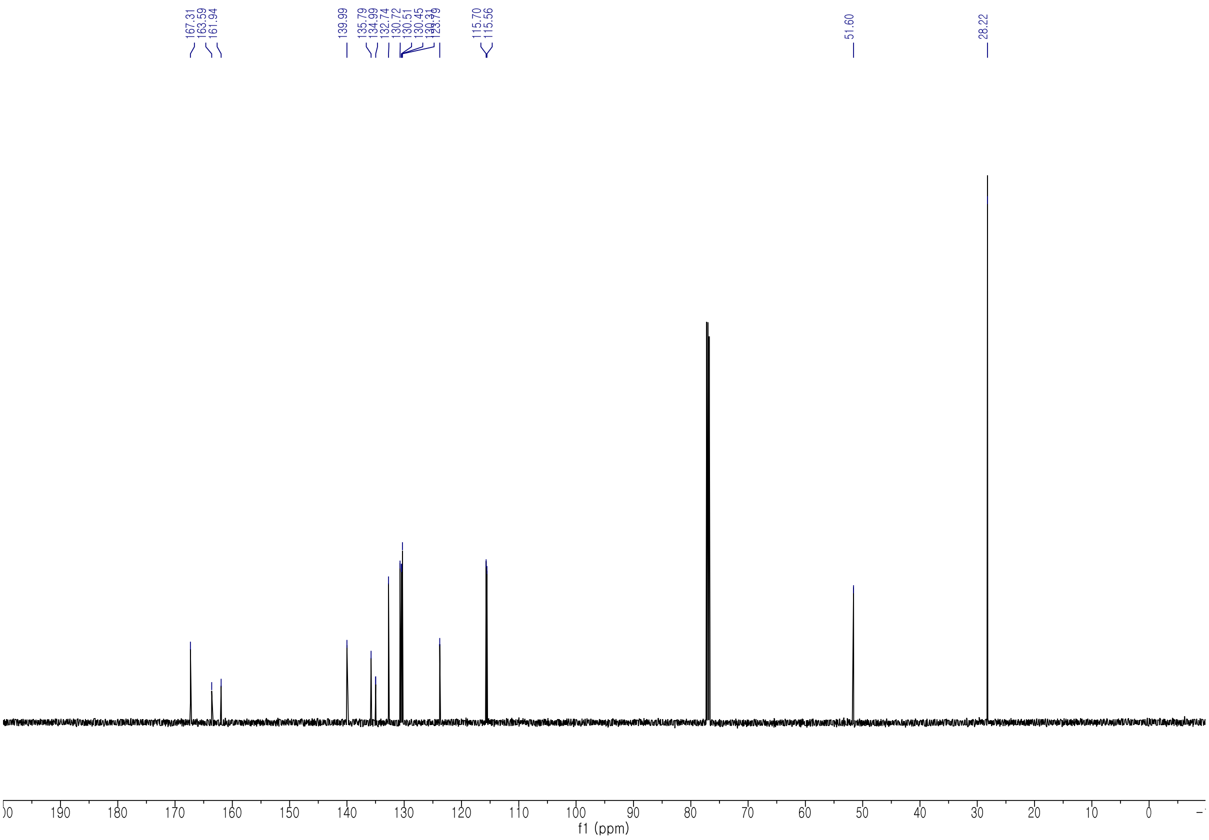


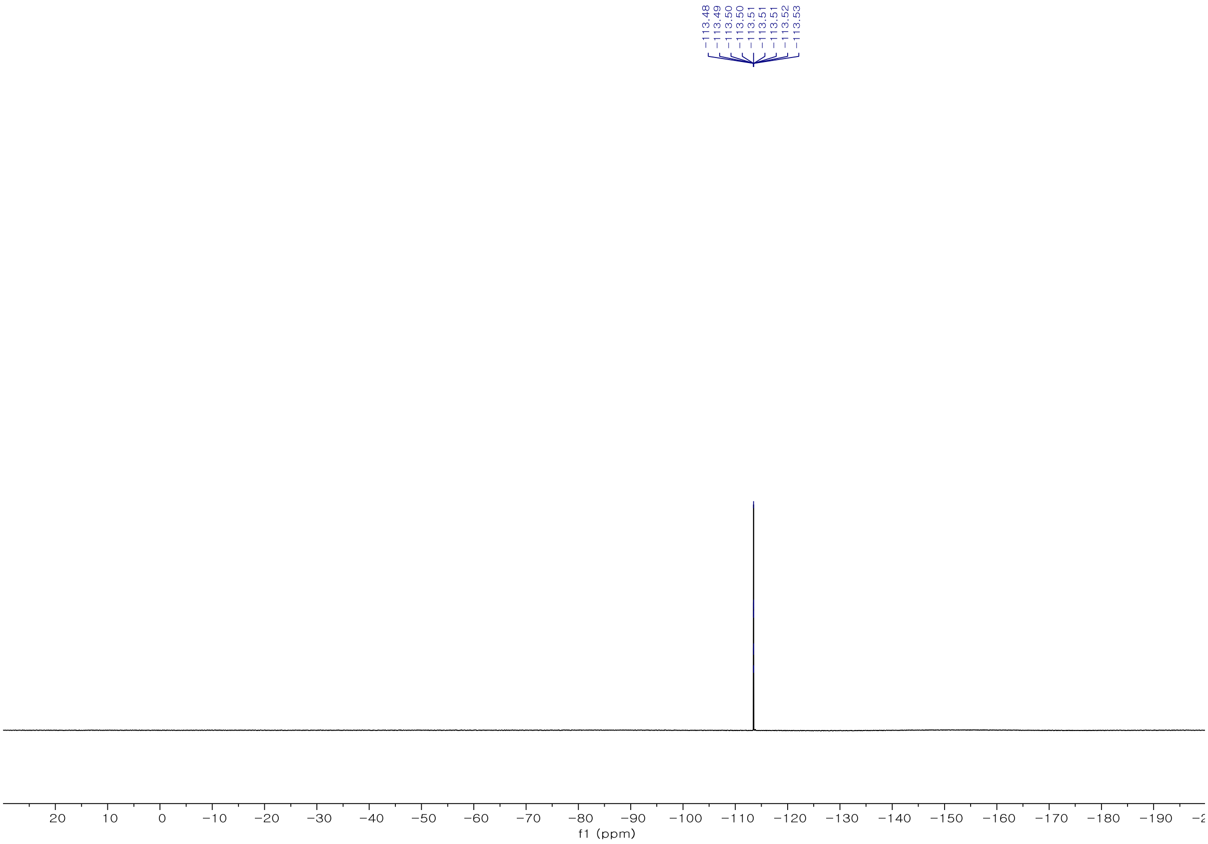


-62.85
-113.28
-113.29
-113.30
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

***N*-(*tert*-Butyl)-4'-fluoro-5-bromo-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3m**)

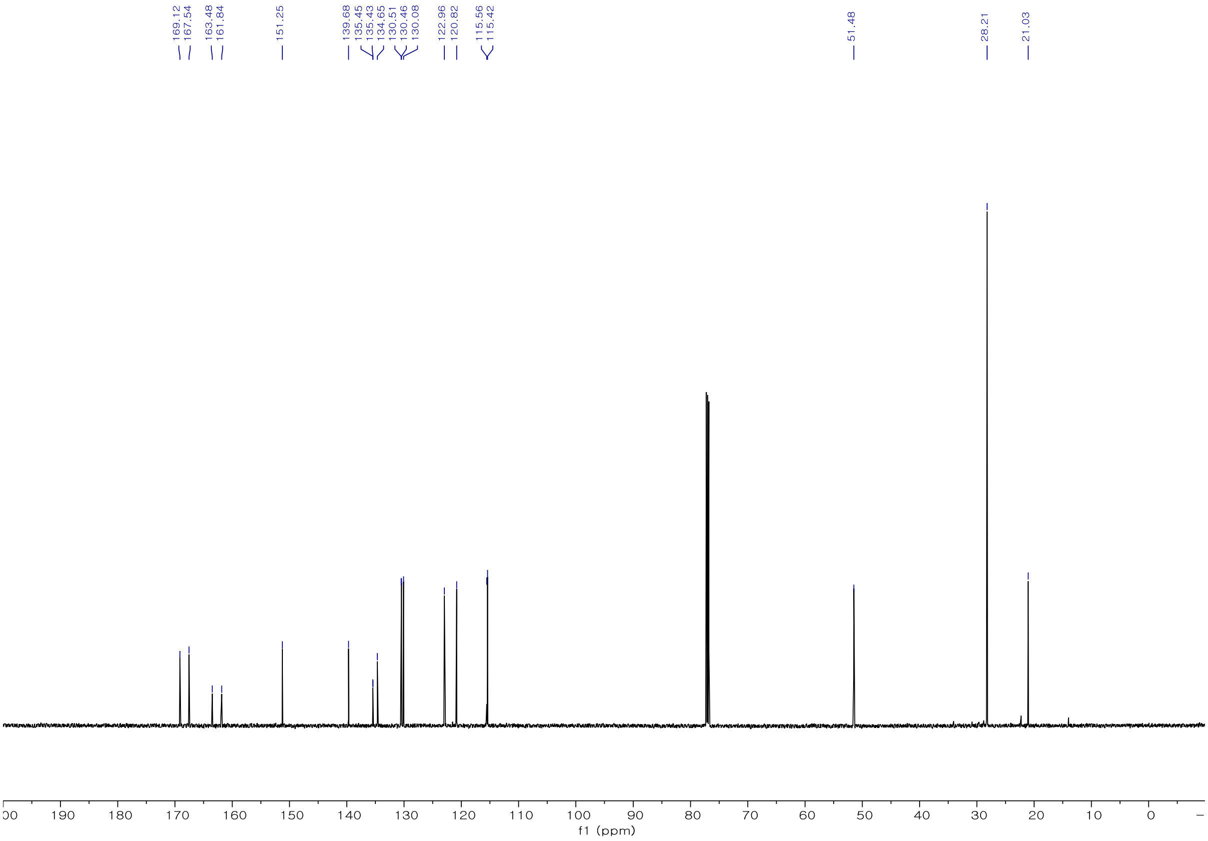


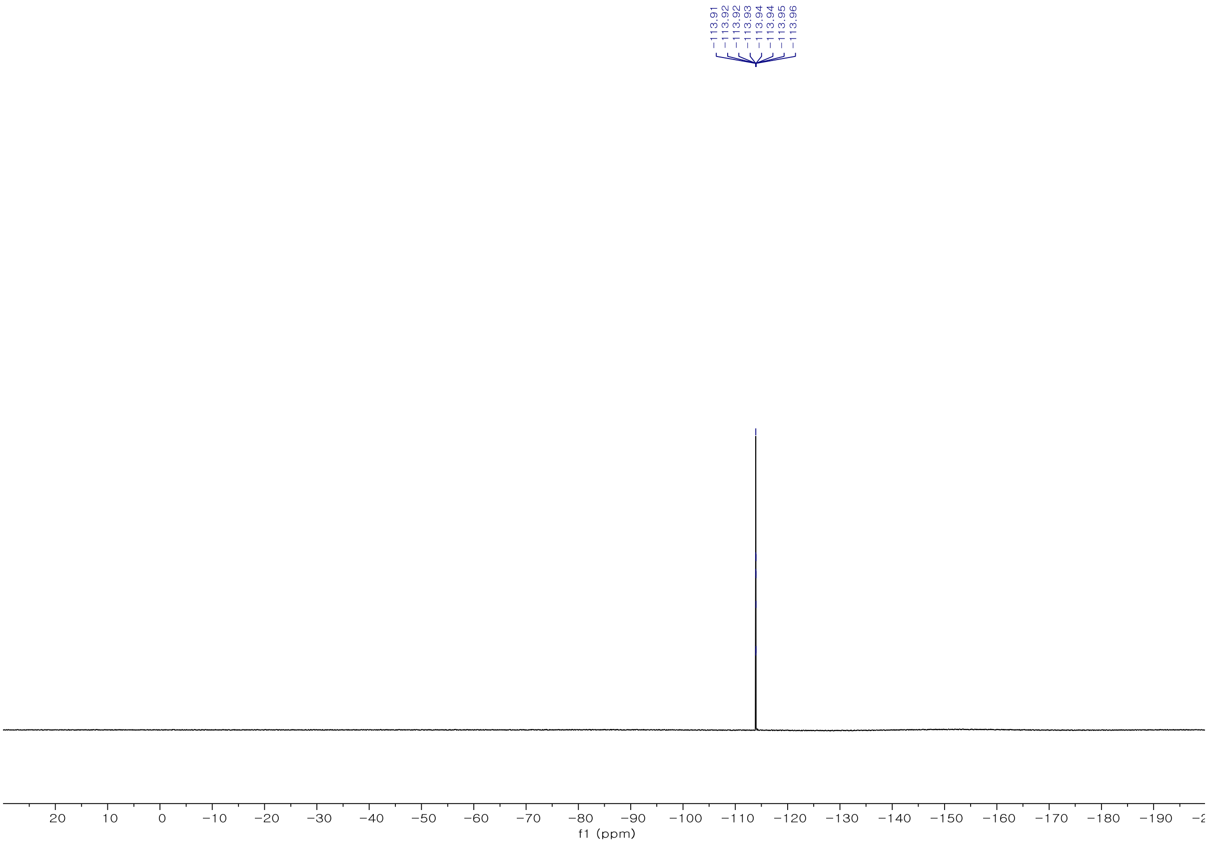




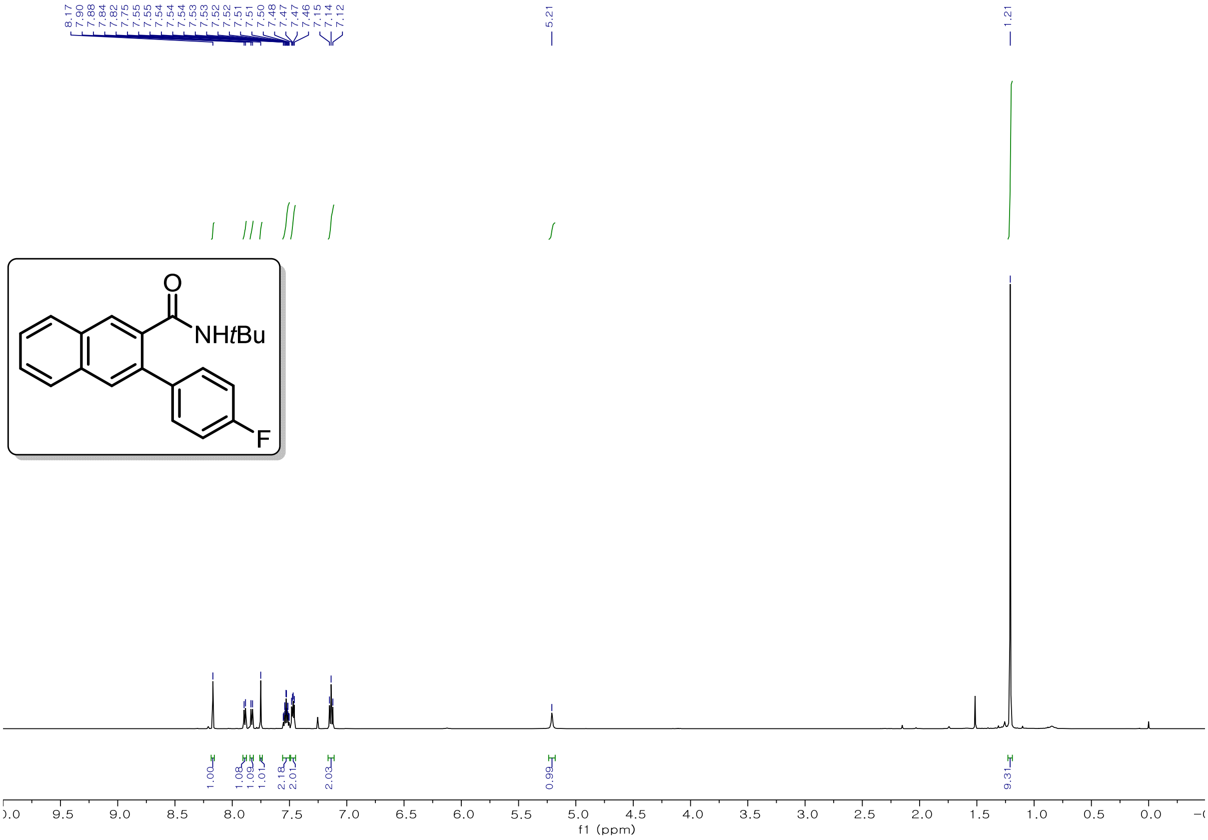
-113.48
-113.49
-113.50
-113.50
-113.51
-113.51
-113.51
-113.52
-113.53
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

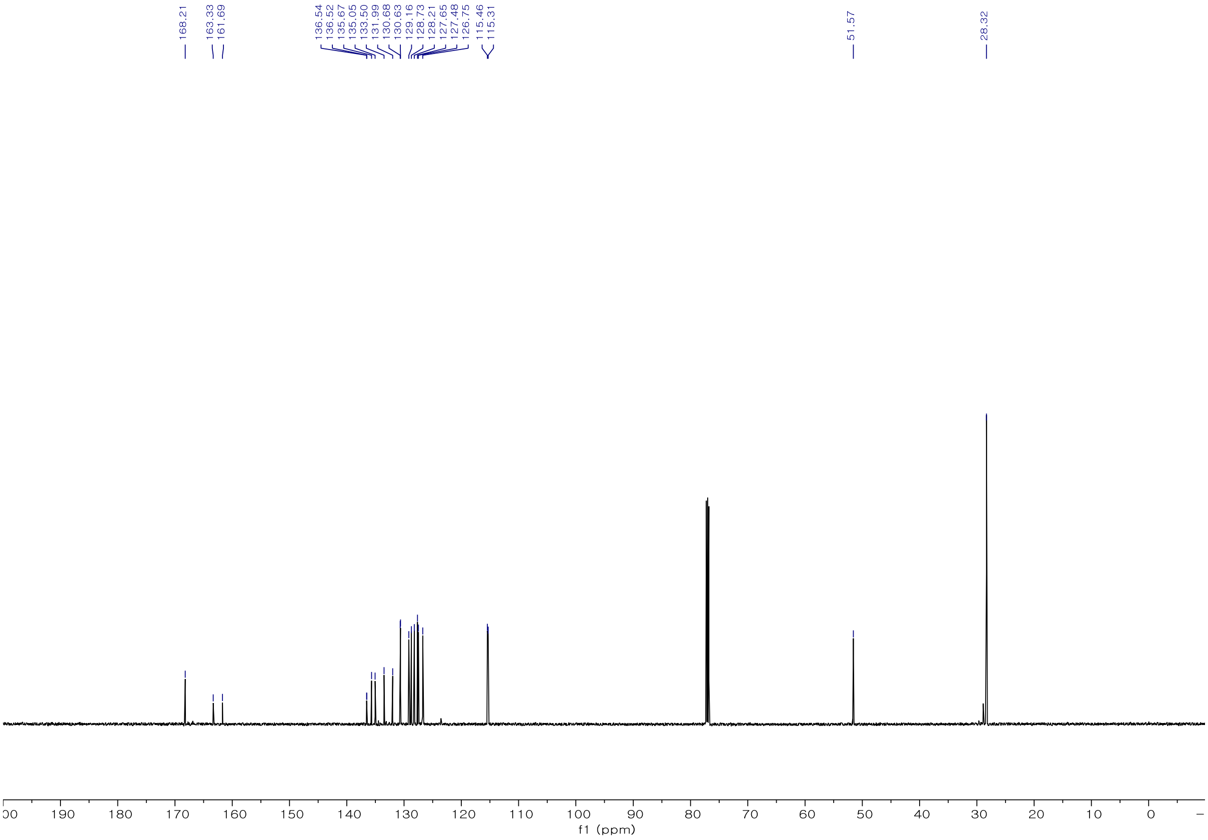
***N*-(*tert*-Butyl)-4'-fluoro-5-acetoxy-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3n**)

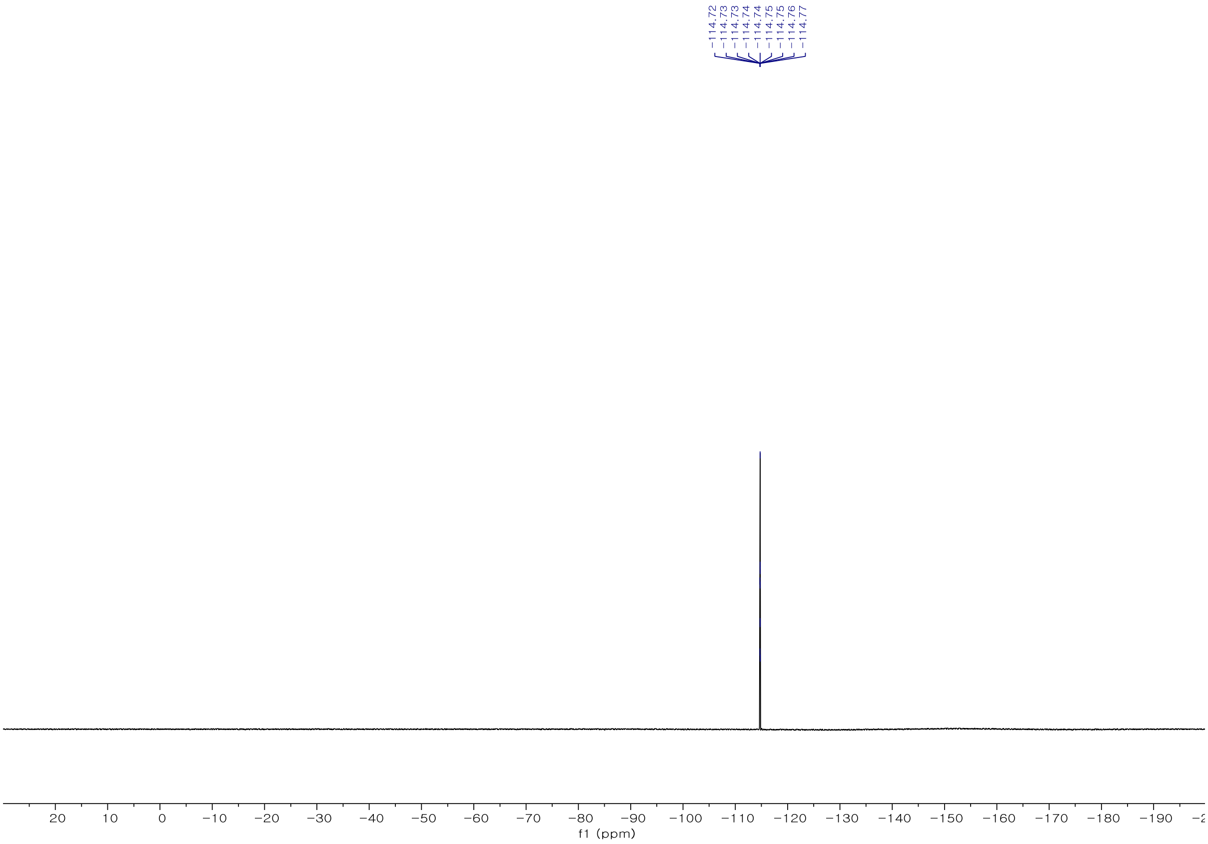



-113.91
-113.92
-113.92
-113.93
-113.94
-113.94
-113.95
-113.96
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

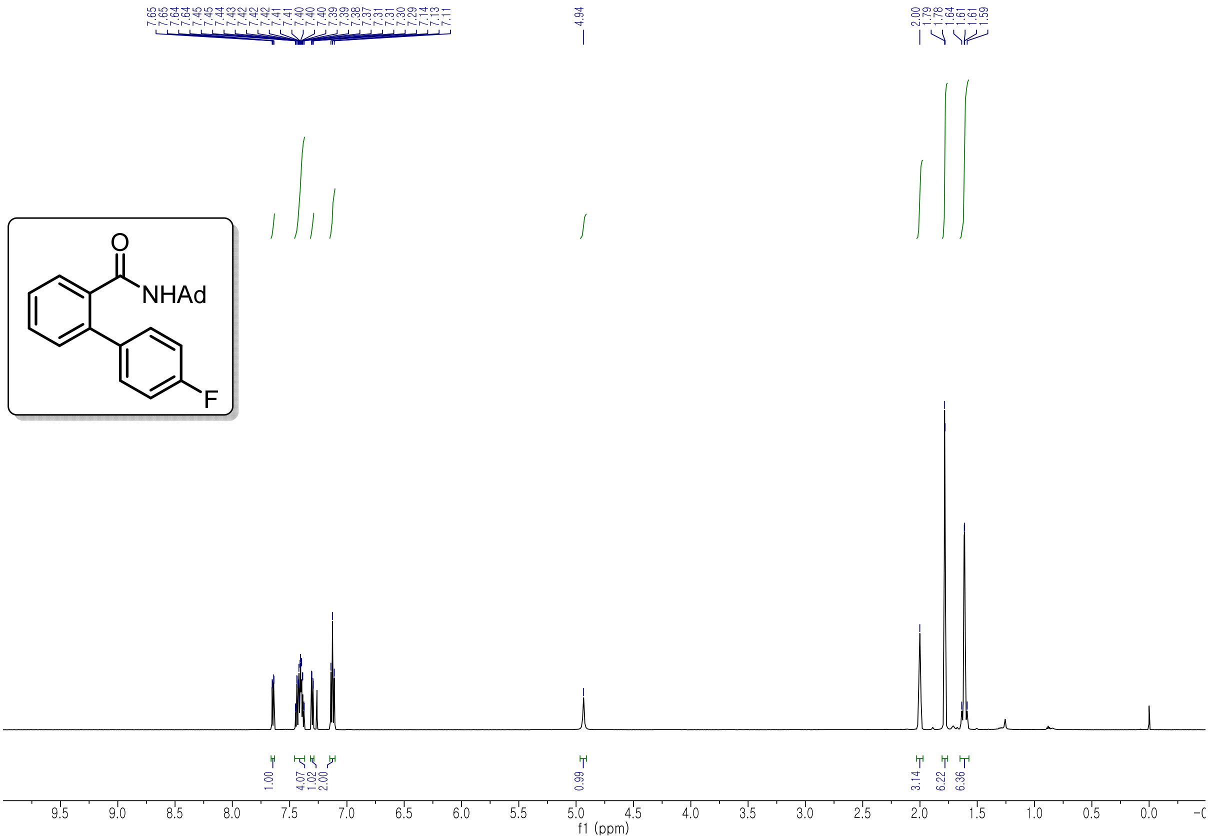
***N*-(*tert*-Butyl)-3-(4-fluorophenyl)-2-naphthamide** (Table 3, **3o**)

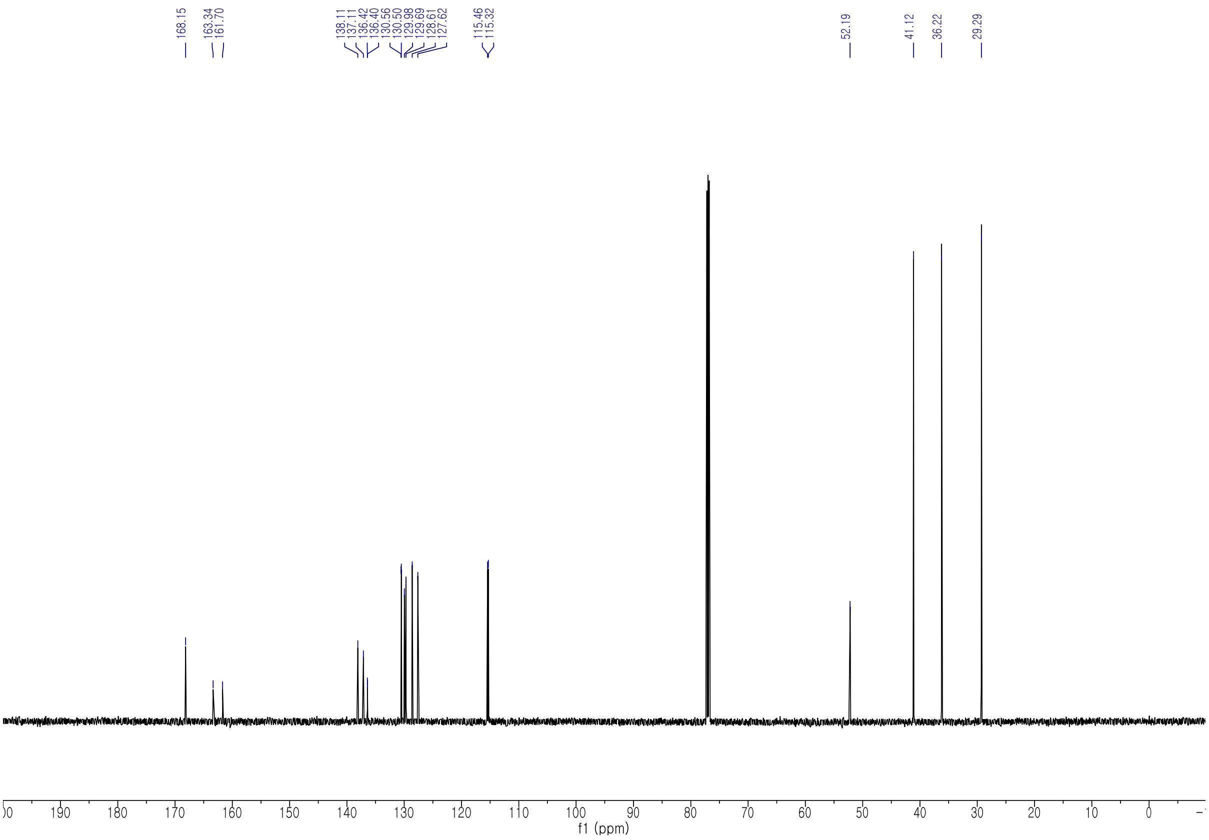


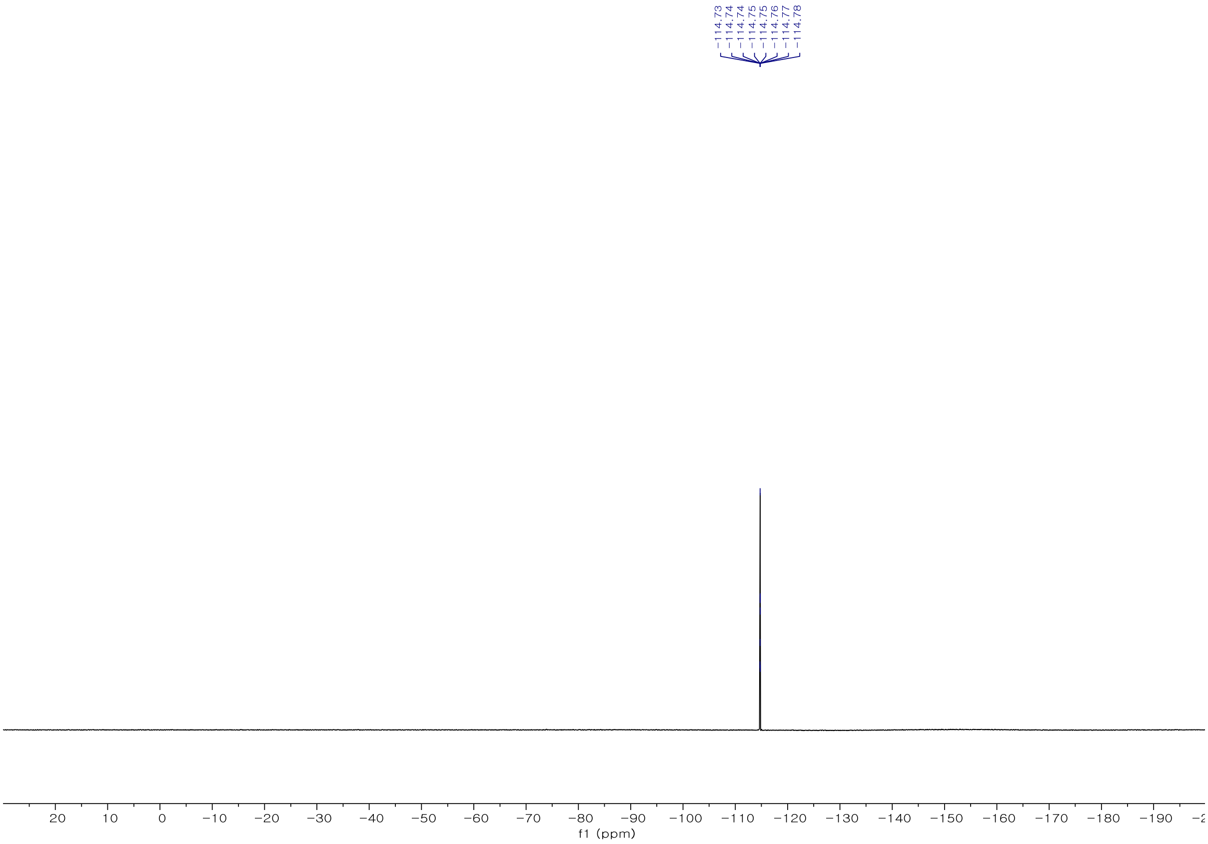



-114.72
-114.73
-114.73
-114.74
-114.74
-114.75
-114.75
-114.76
-114.77
f1 (ppm)

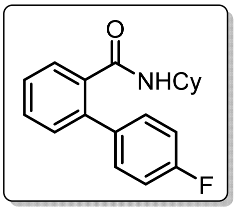
***N*-Adamantanyl-4'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3p**)

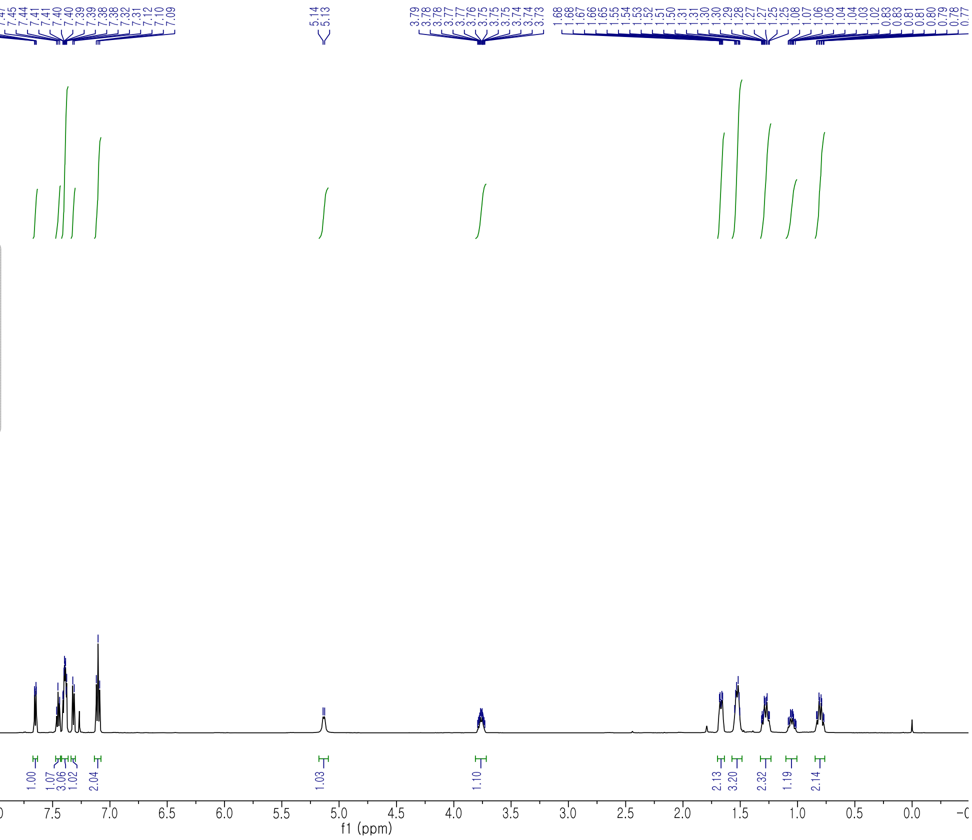


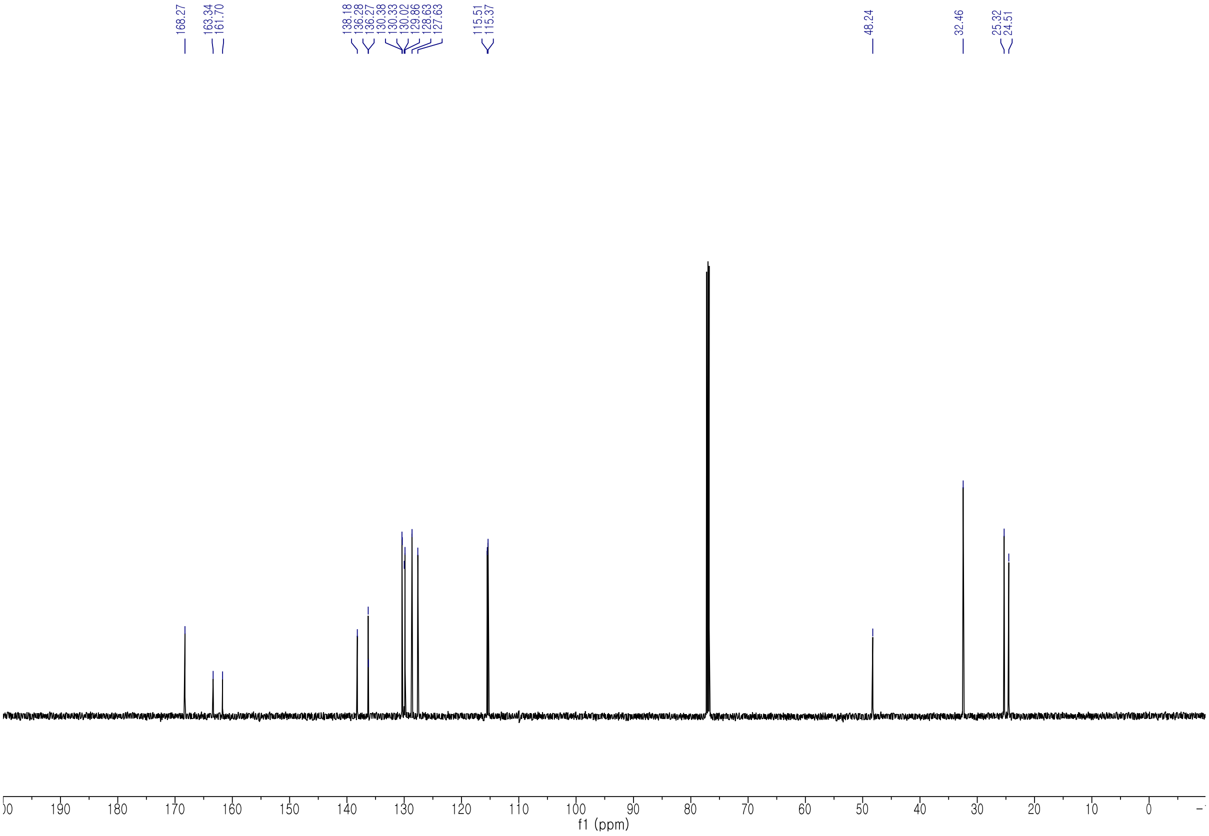


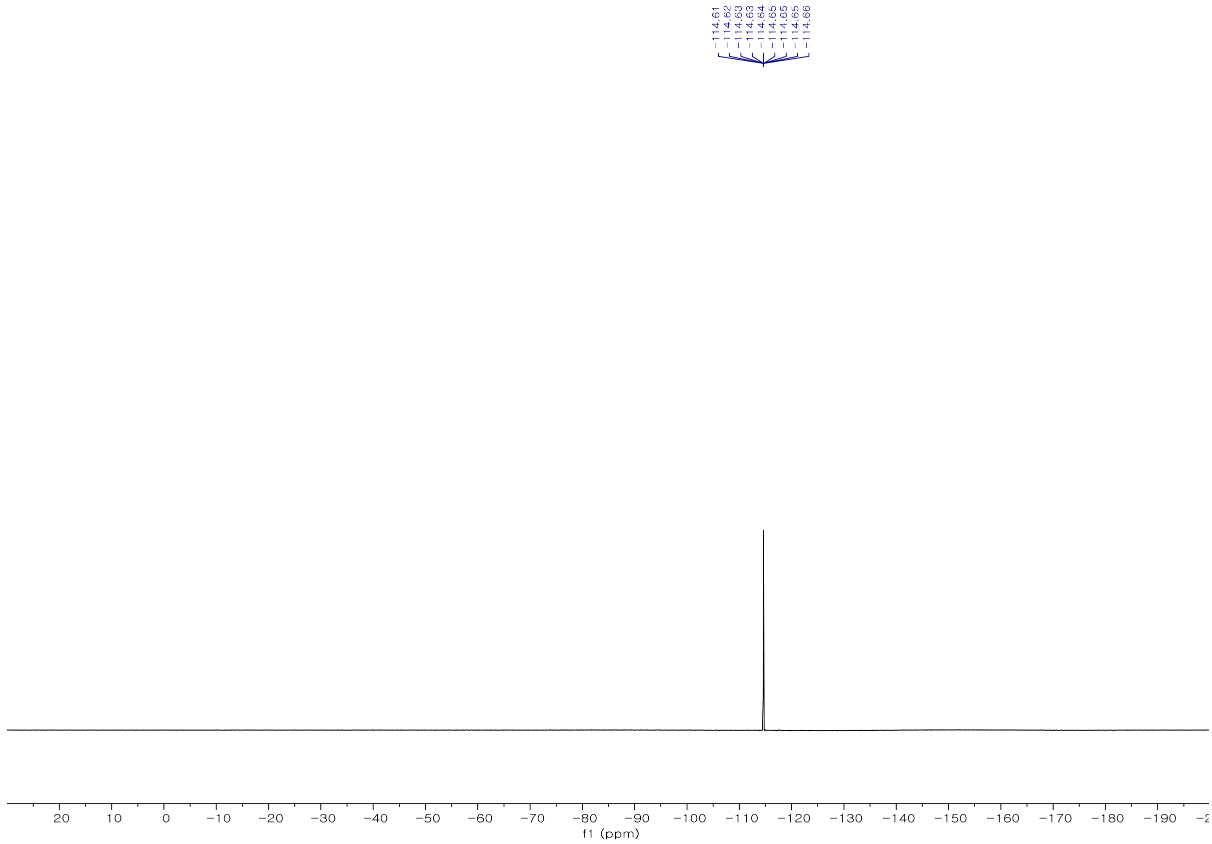

-114.73
-114.74
-114.74
-114.75
-114.75
-114.76
-114.77
-114.78
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

***N*-Cyclohexyl-4'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3q**)

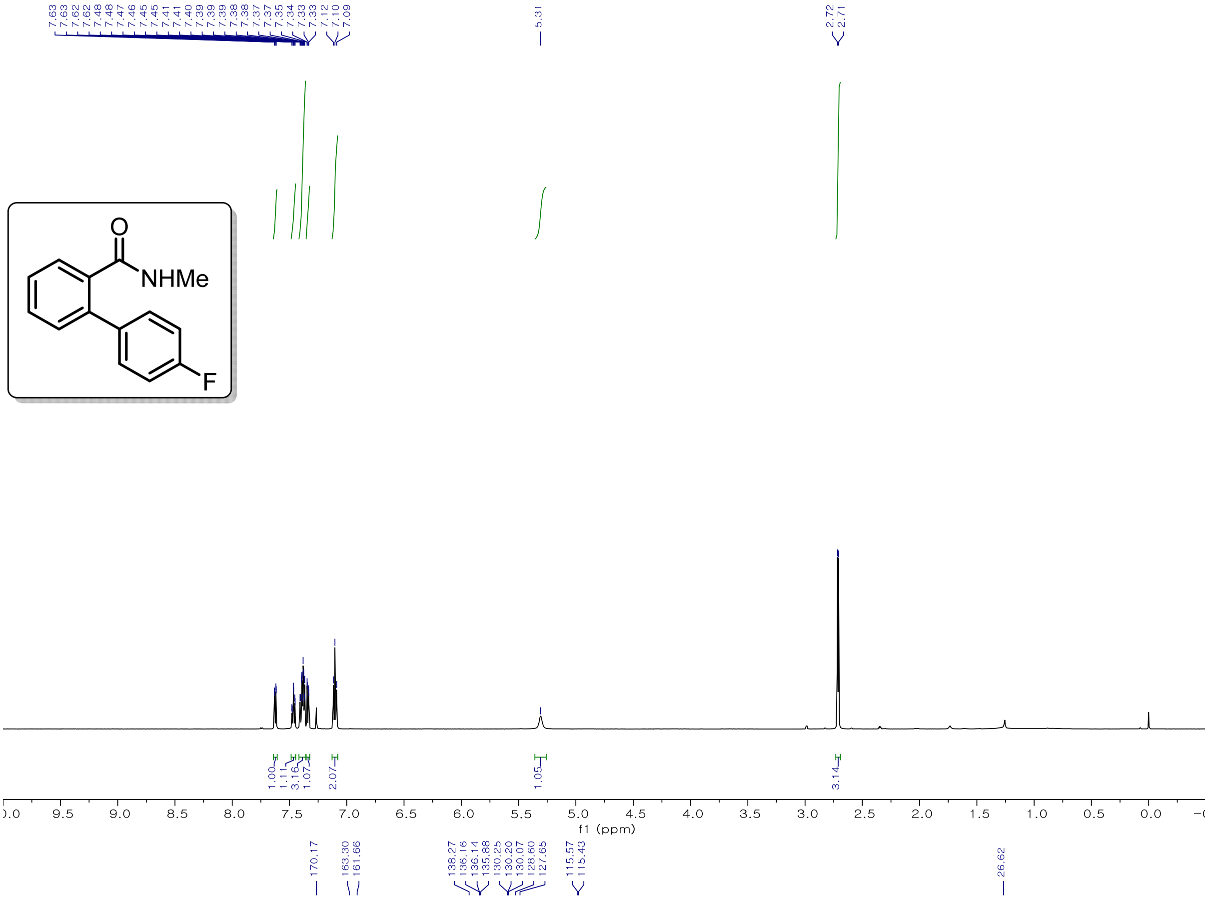


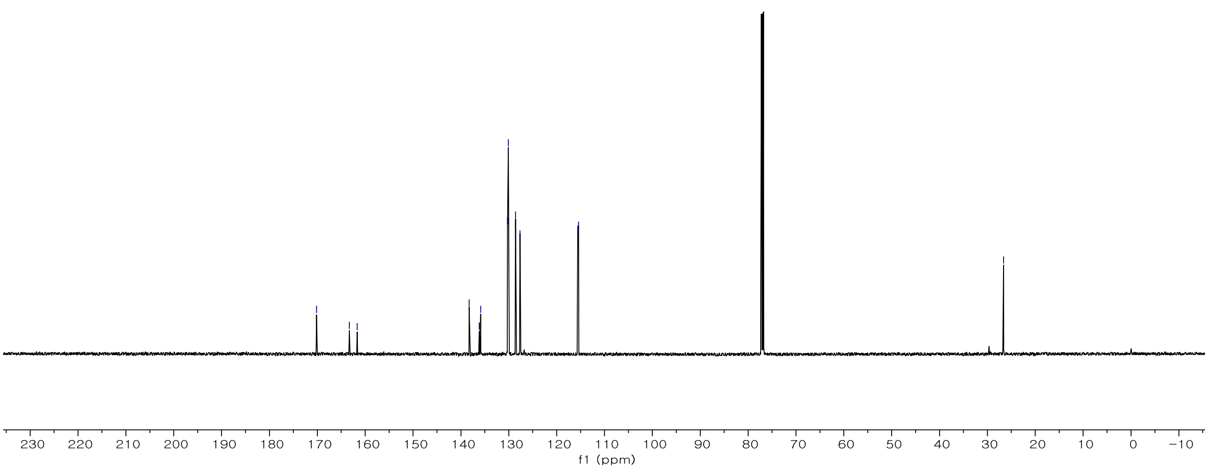


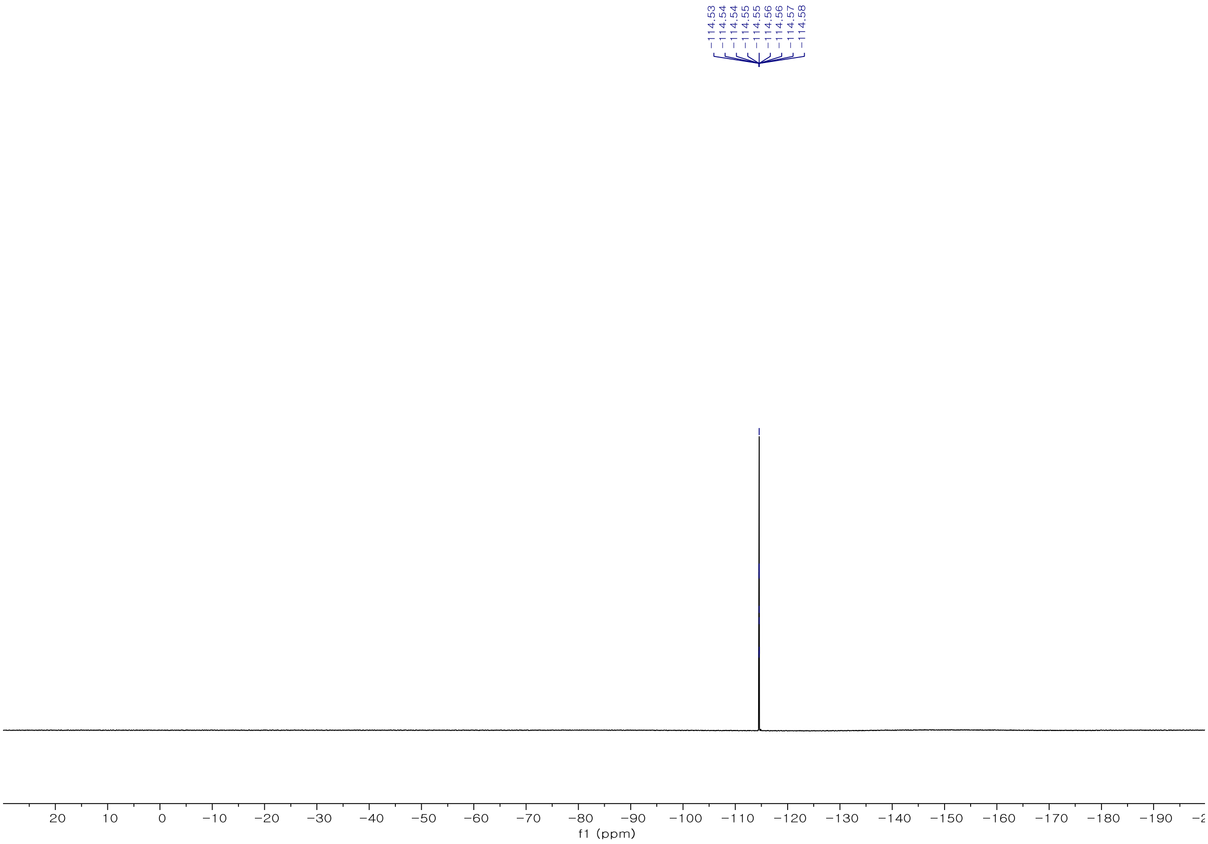



-114.61
-114.62
-114.63
-114.63
-114.64
-114.65
-114.65
-114.65
-114.66
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

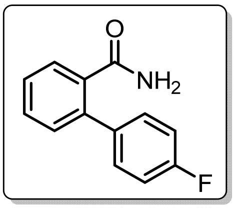
***N*-Methyl-4'-fluoro-[1,1'-biphenyl]-2-carboxamide** (Table 3, **3r**)

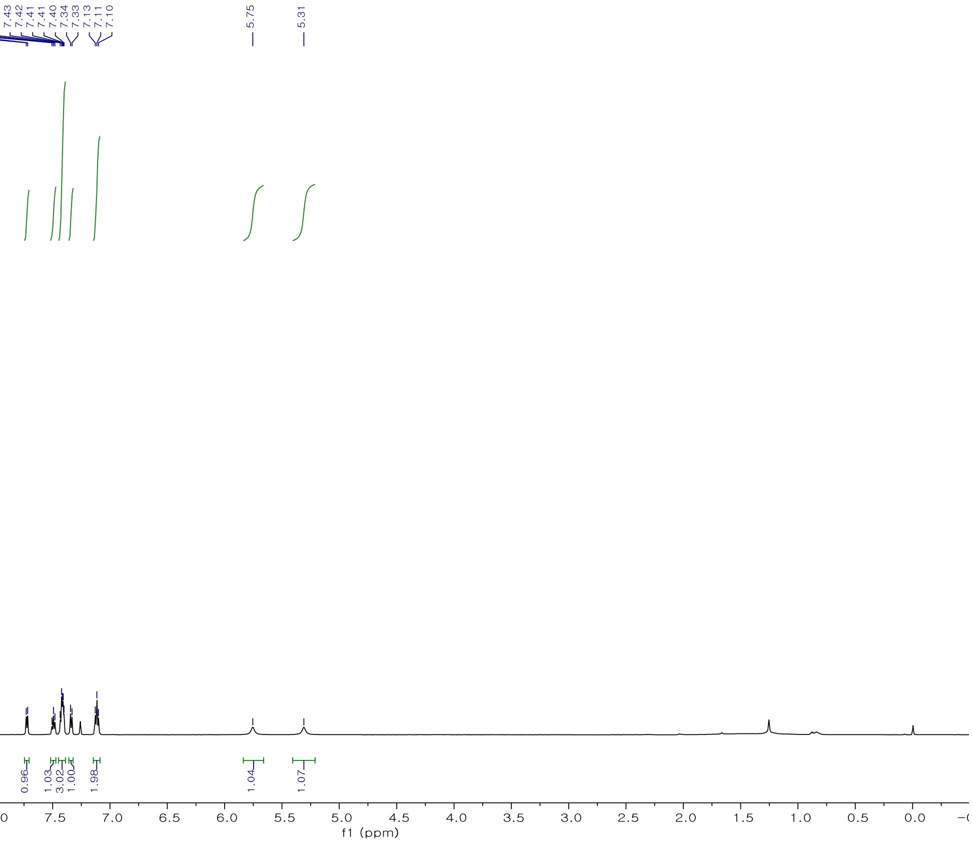


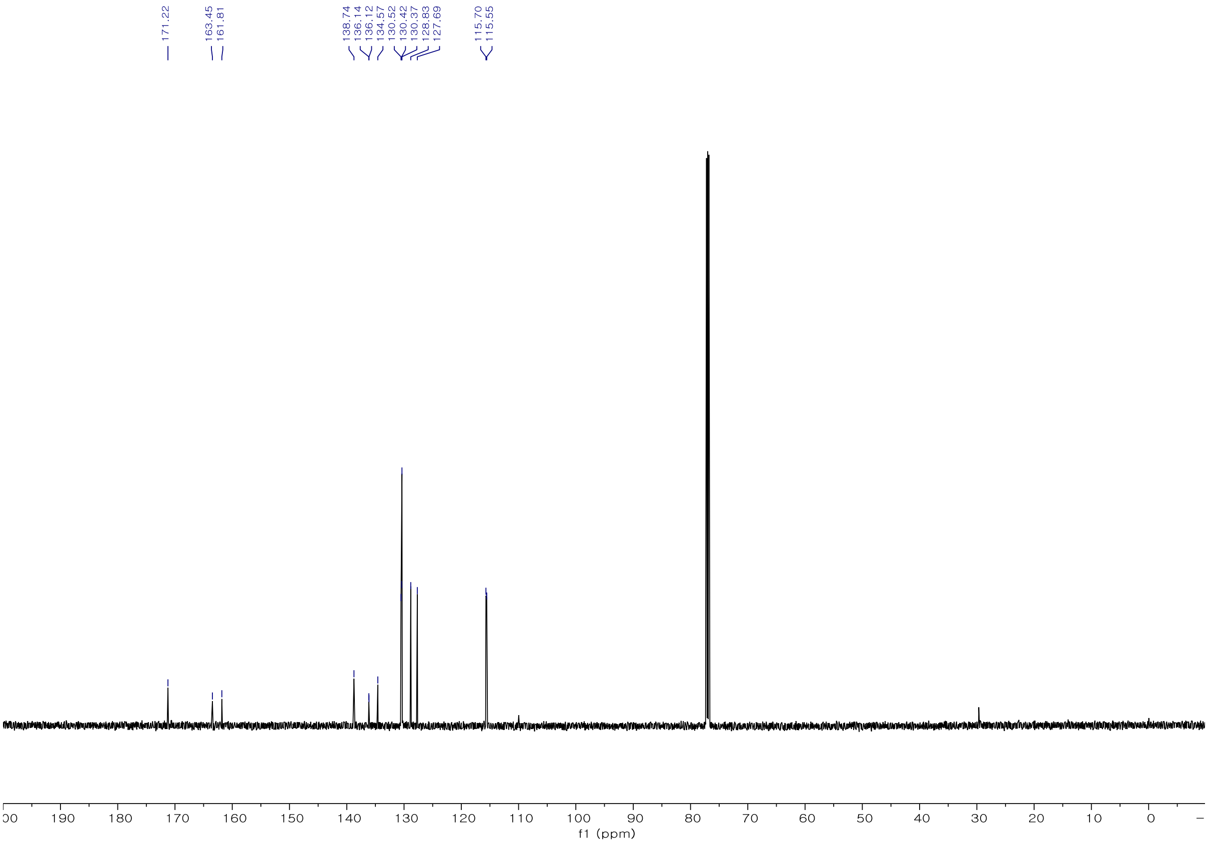


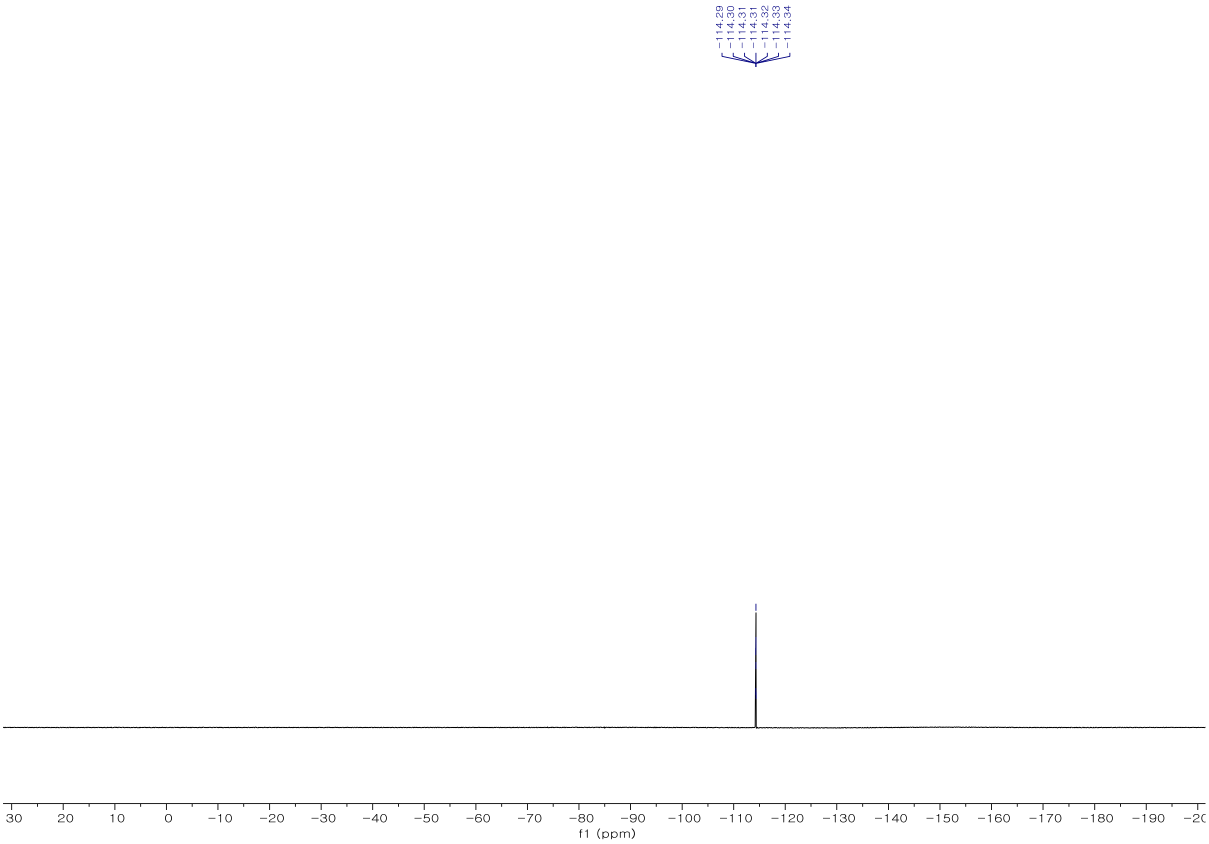

-114.53
-114.54
-114.54
-114.55
-114.55
-114.56
-114.56
-114.57
-114.58
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

4'-Fluoro-[1,1'-biphenyl]-2-carboxamide (Table 3, **3s**)

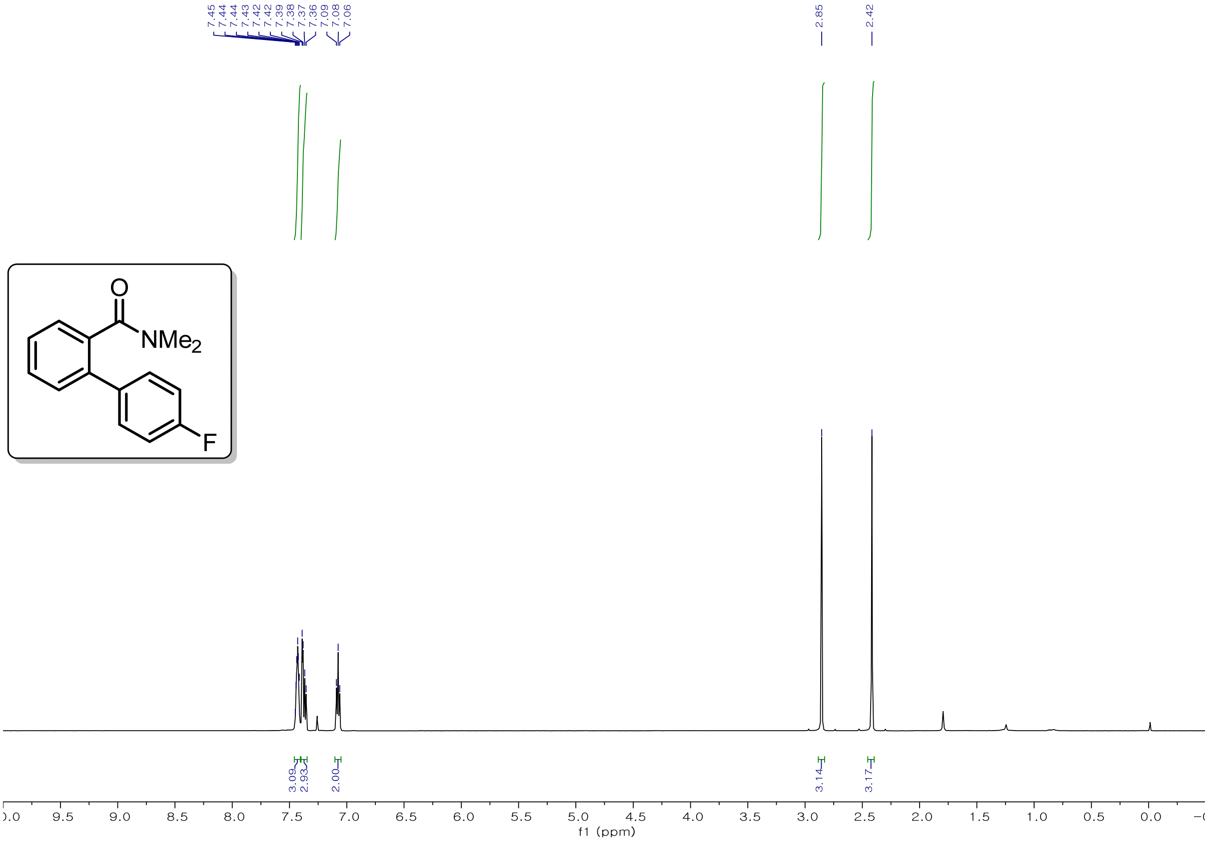


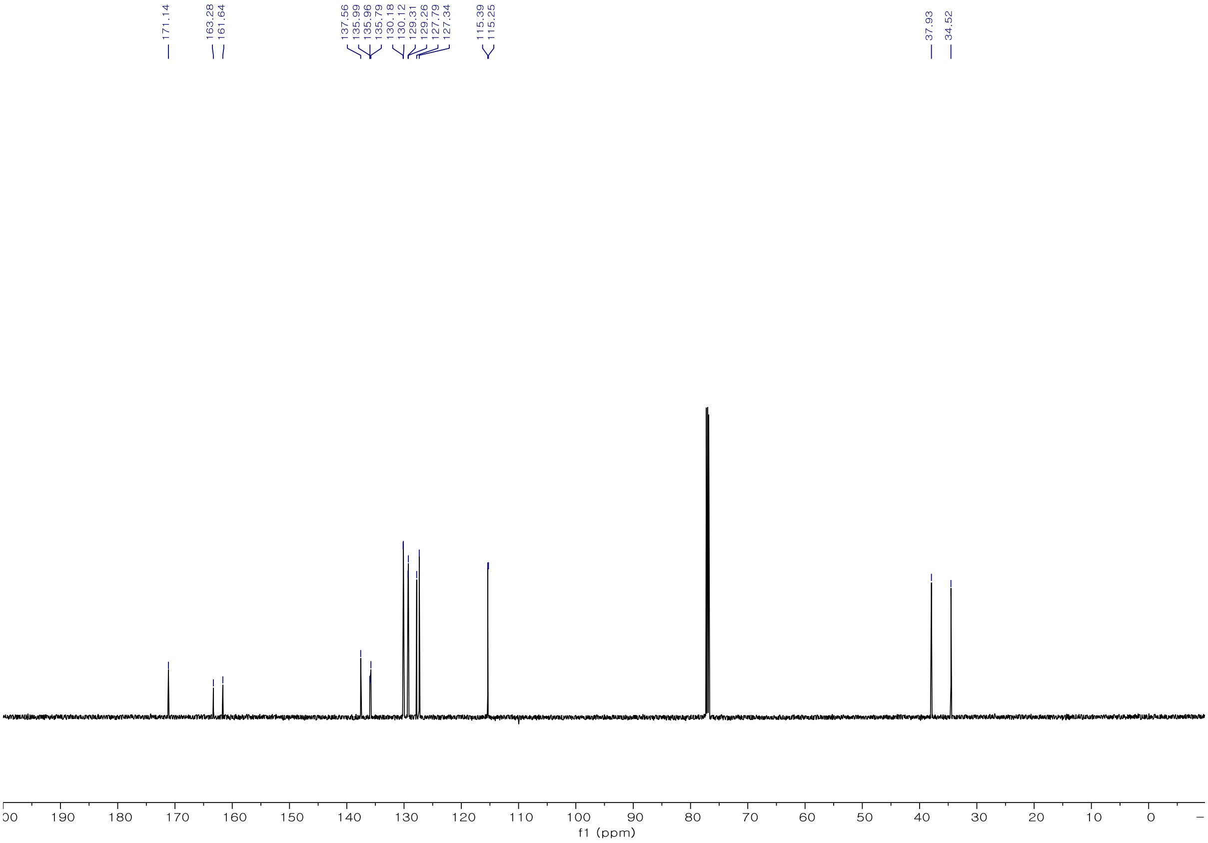


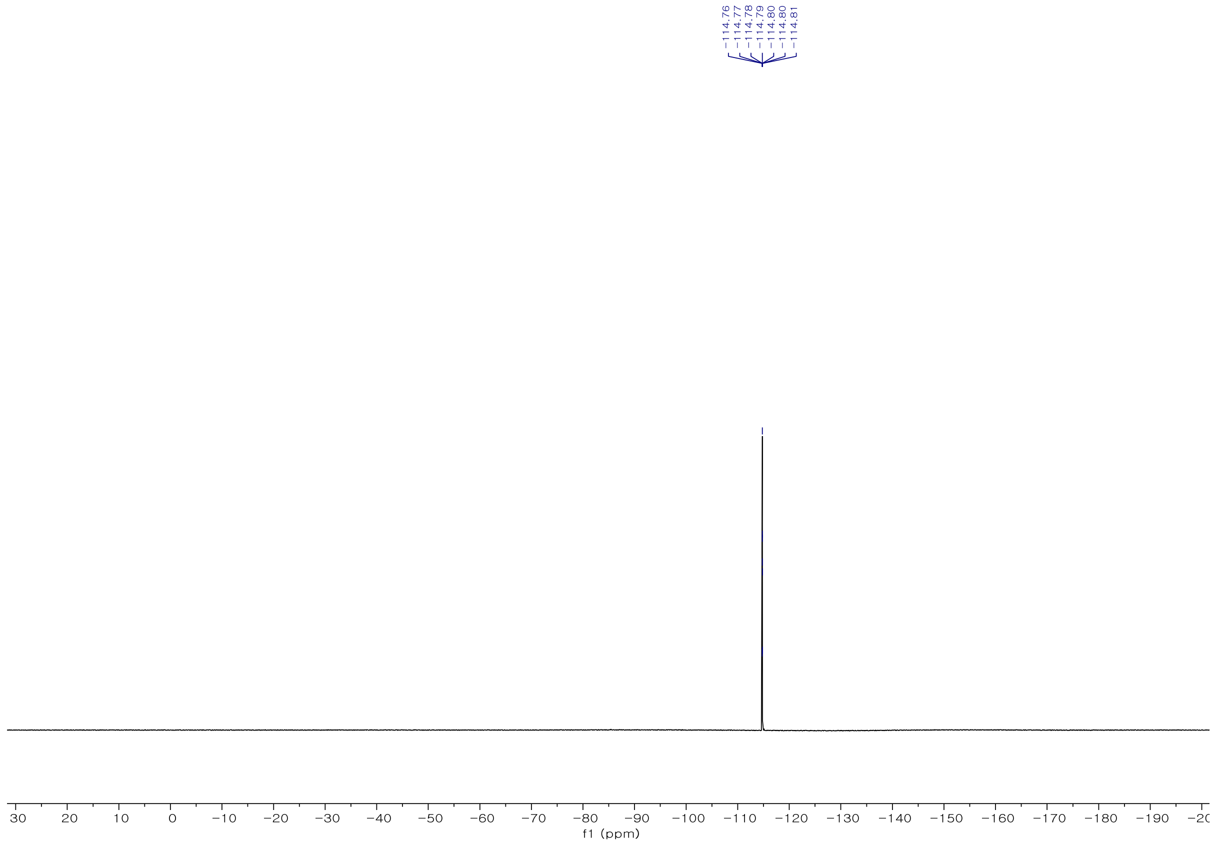



-114.29
-114.30
-114.31
-114.31
-114.32
-114.33
-114.34
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

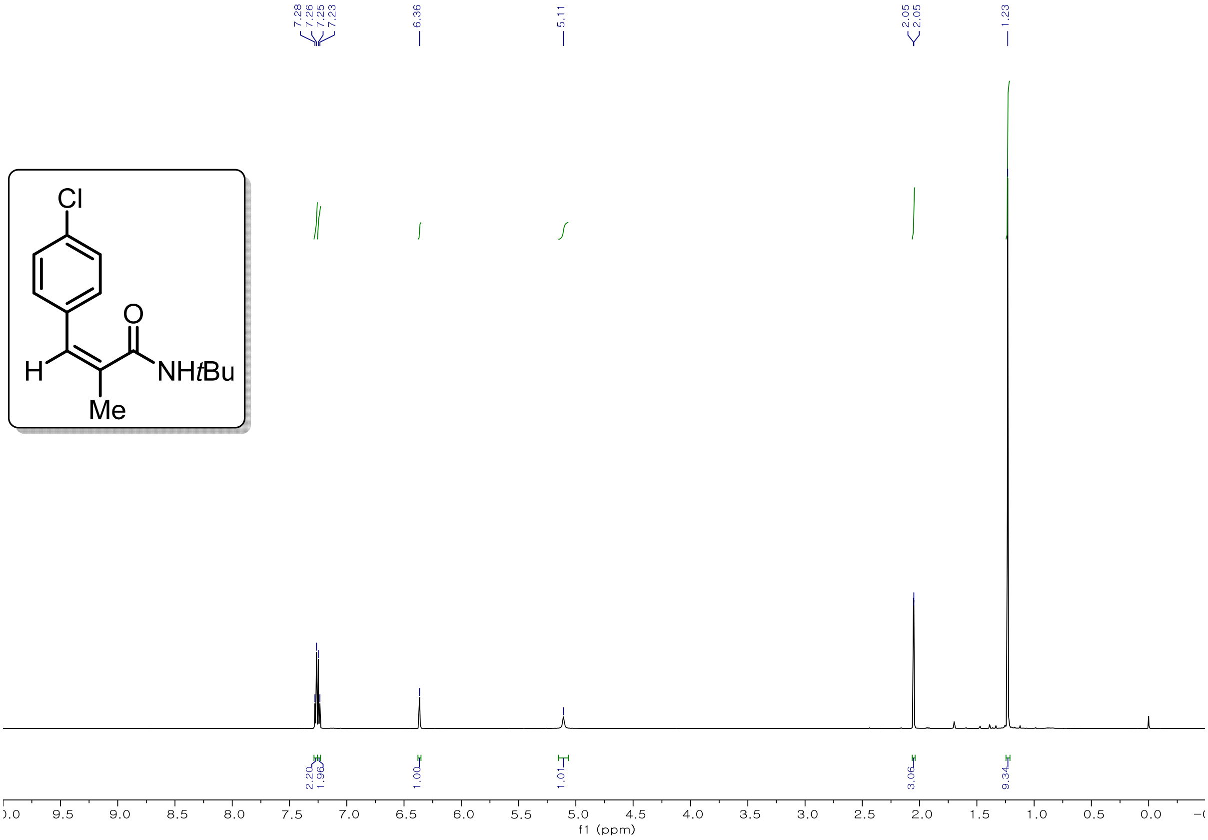
4'-Fluoro-*N,N*-dimethyl-[1,1'-biphenyl]-2-carboxamide (Table 3, **3t**)

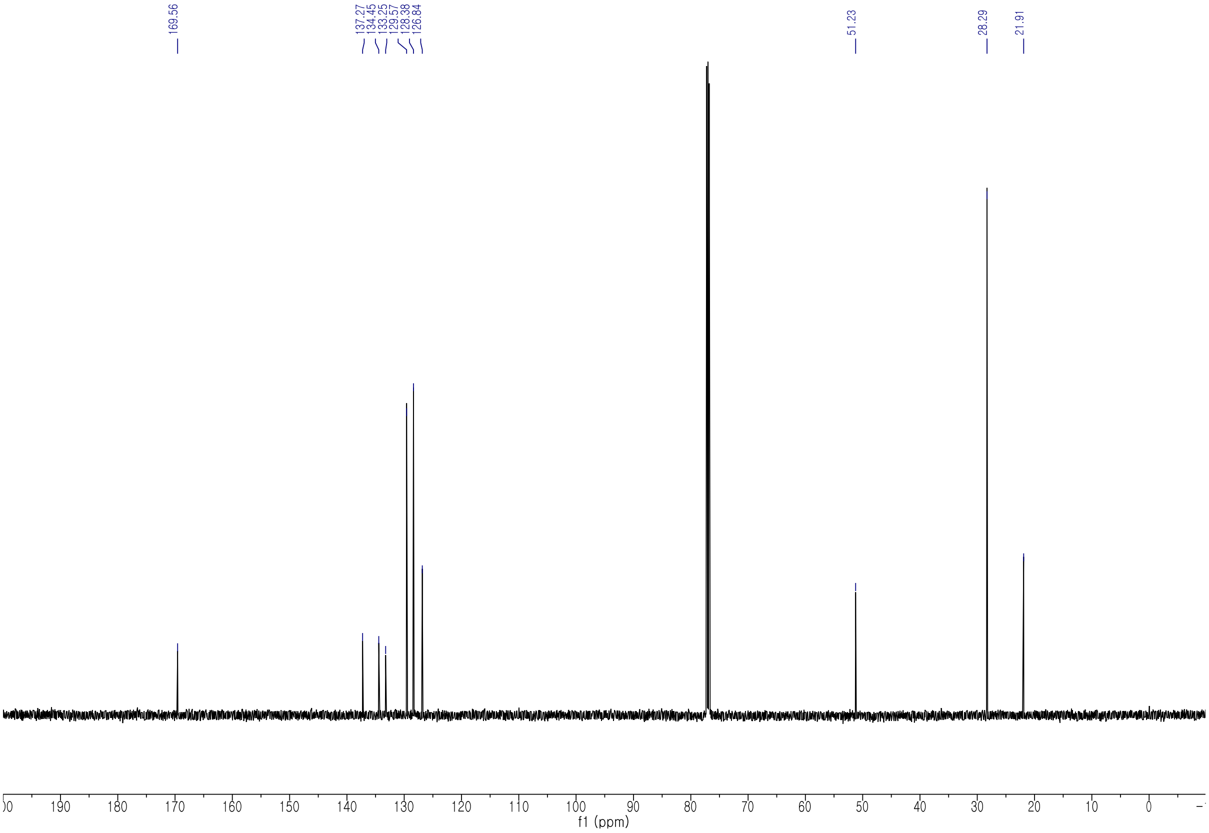




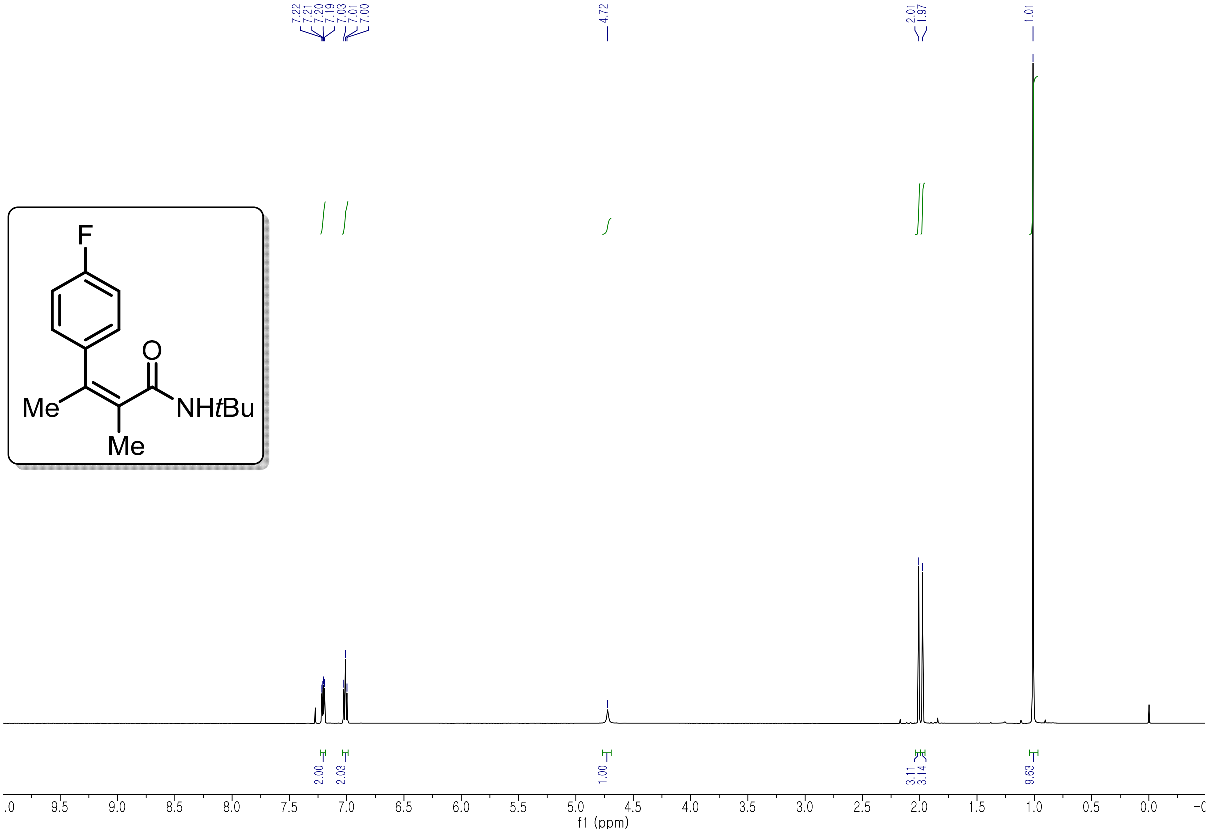

-114.76
-114.77
-114.78
-114.79
-114.80
-114.80
-114.81
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20
f1 (ppm)

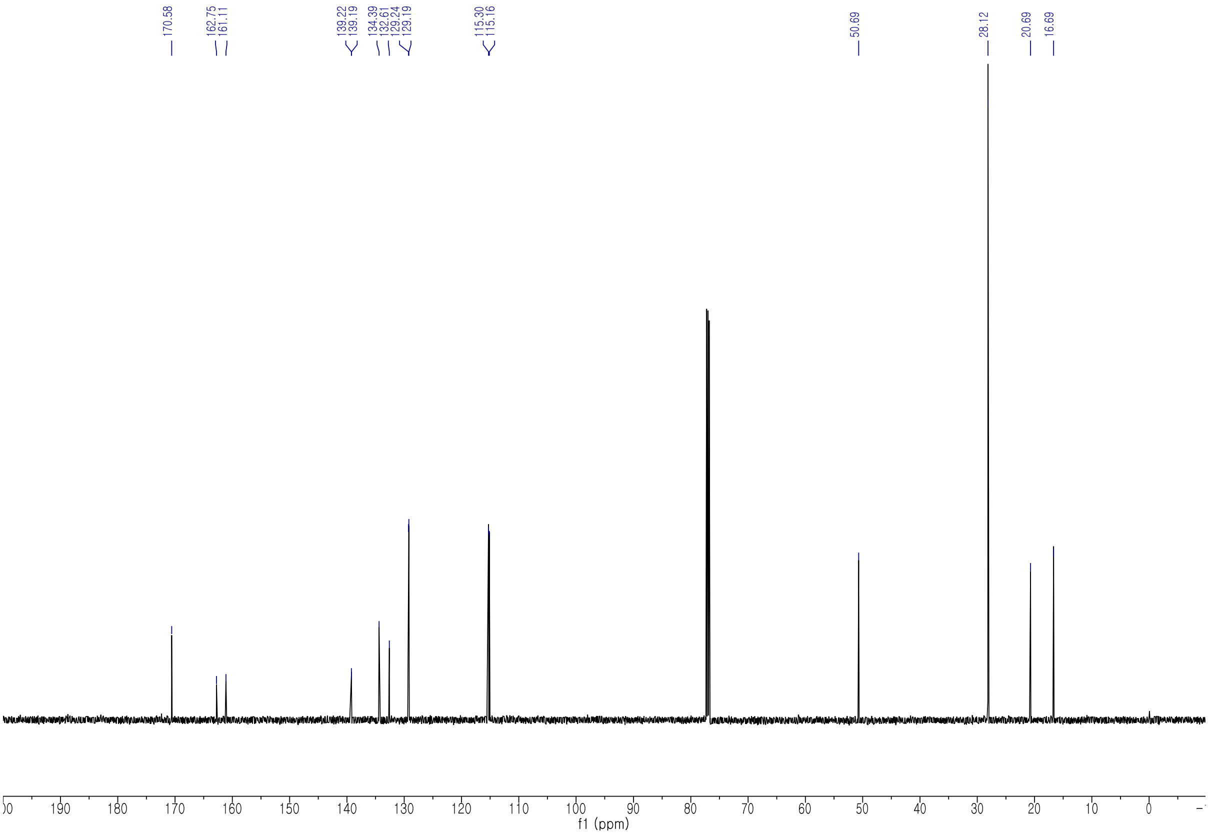
***(Z)-N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methylacrylamide** (Table 4, **5a**)

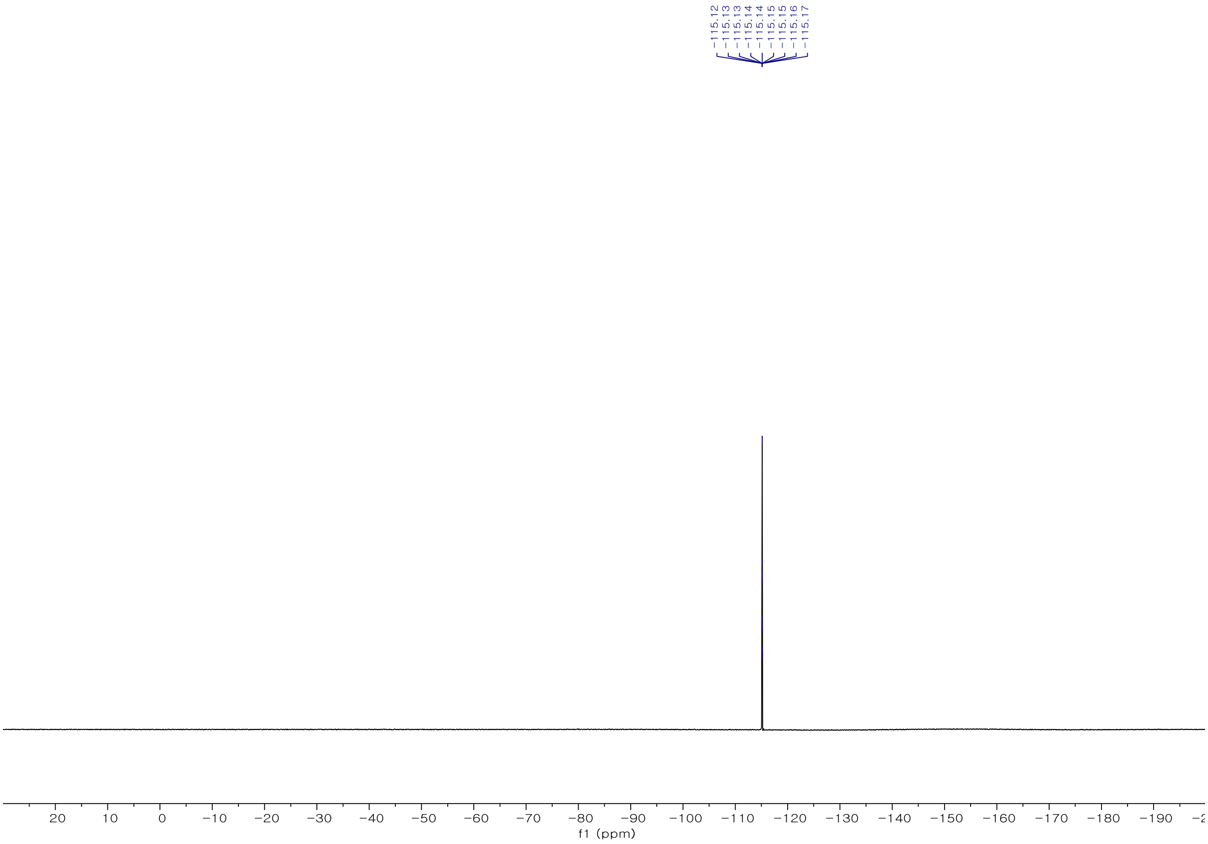




***(Z)-N*-(*tert*-Butyl)-3-(4-fluorophenyl)-2-methylbut-2-enamide** (Table 4, **5b**)

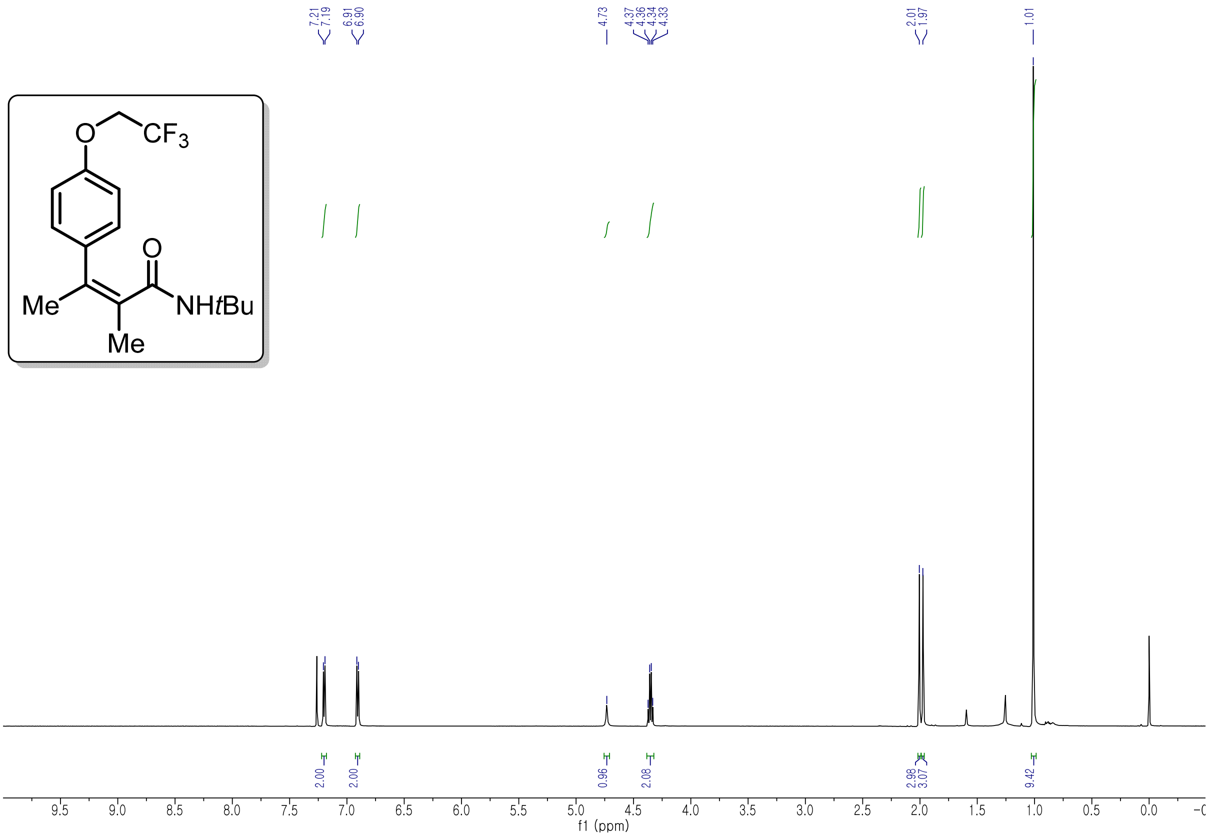


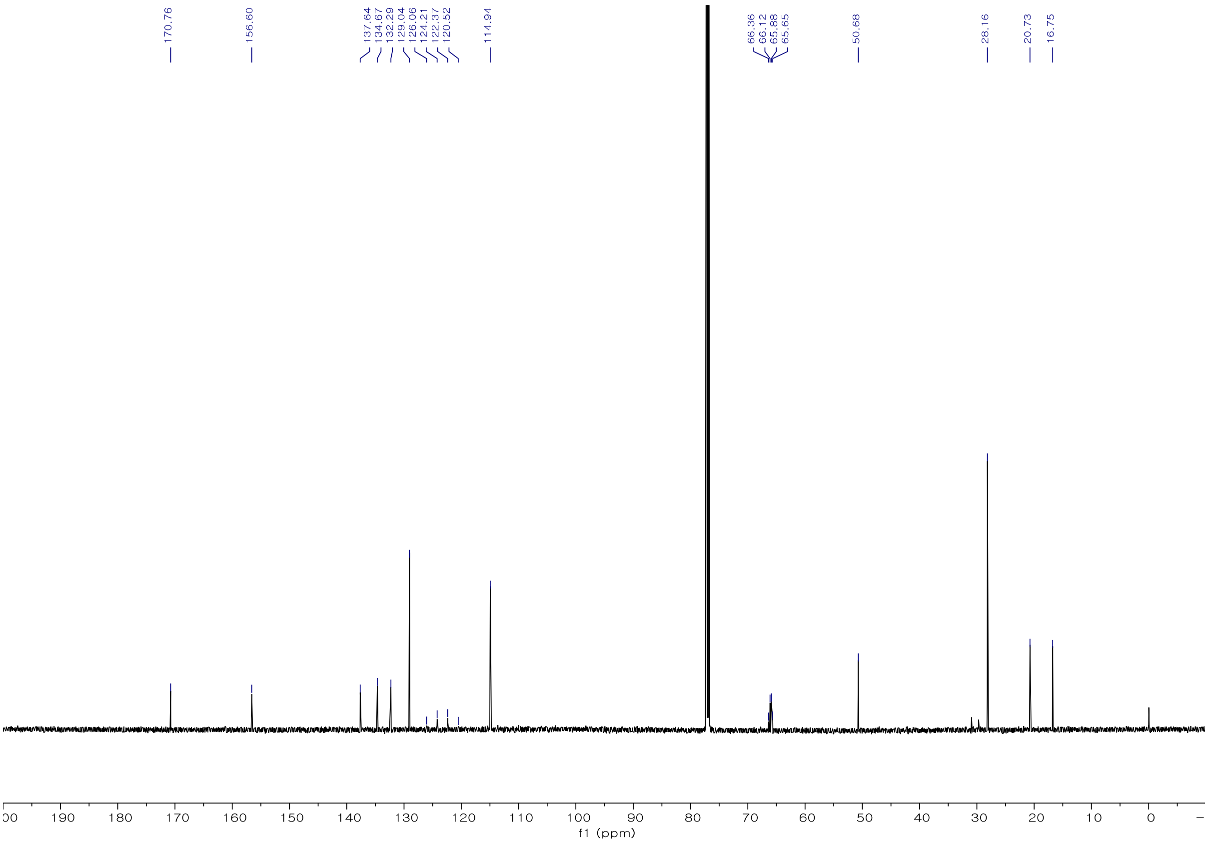


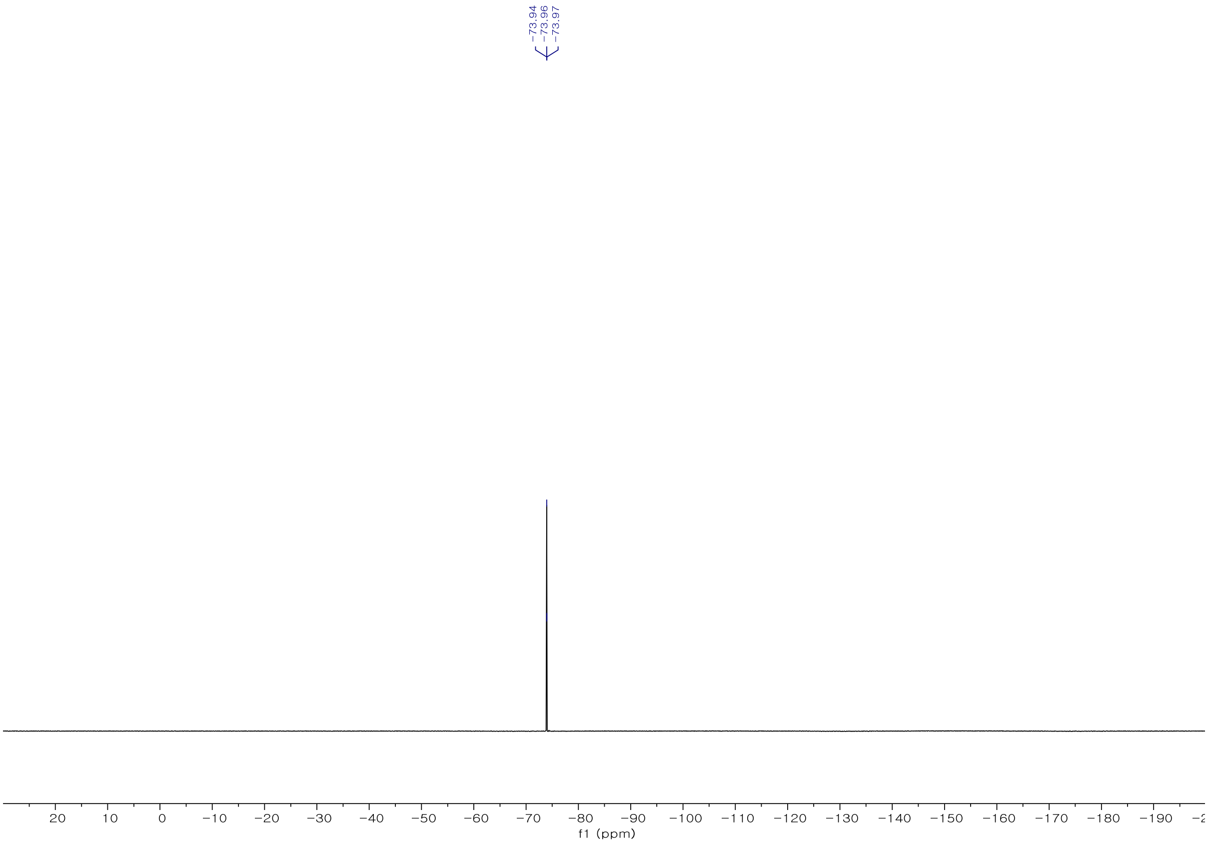


-115.12
-115.13
-115.13
-115.14
-115.14
-115.15
-115.15
-115.16
-115.17
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

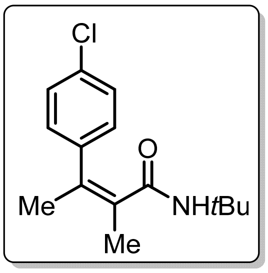
***(Z)*-*N*-(*tert*-Butyl)-2-methyl-3-[4-(2,2,2-trifluoroethoxy)phenyl]but-2-enamide** (Table 4, **5b’**)

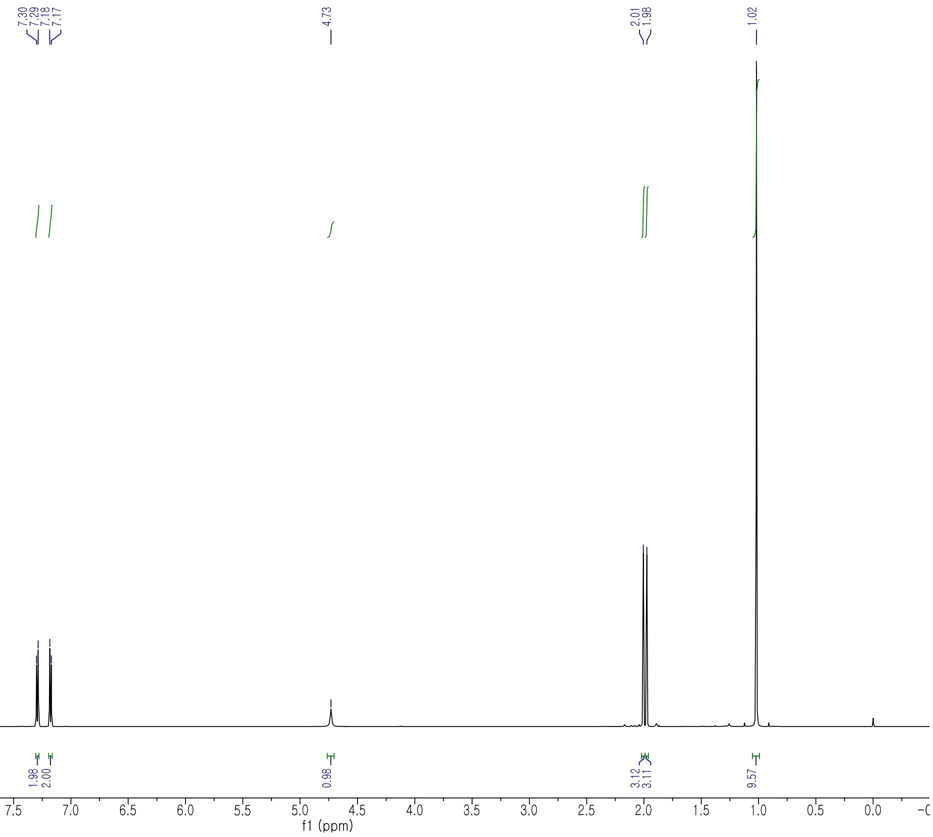


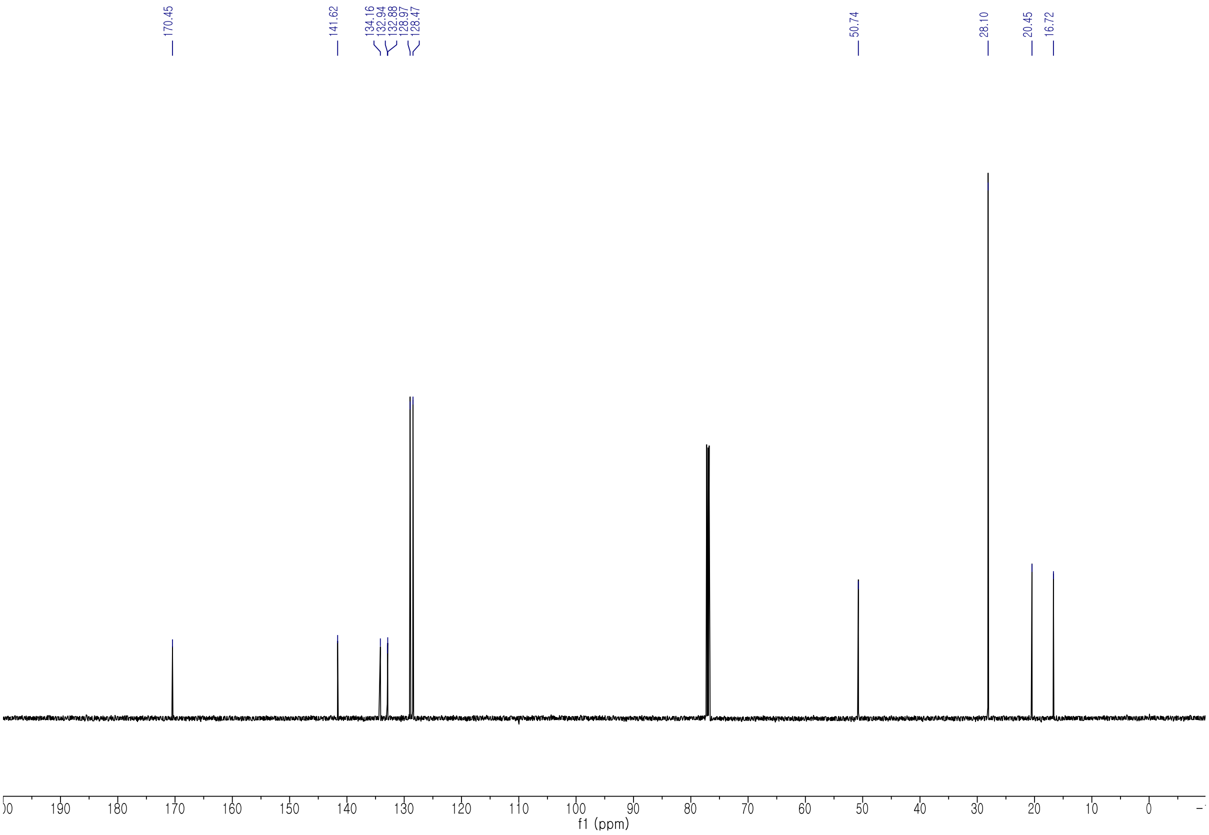



-73.94
-73.96
-73.97
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

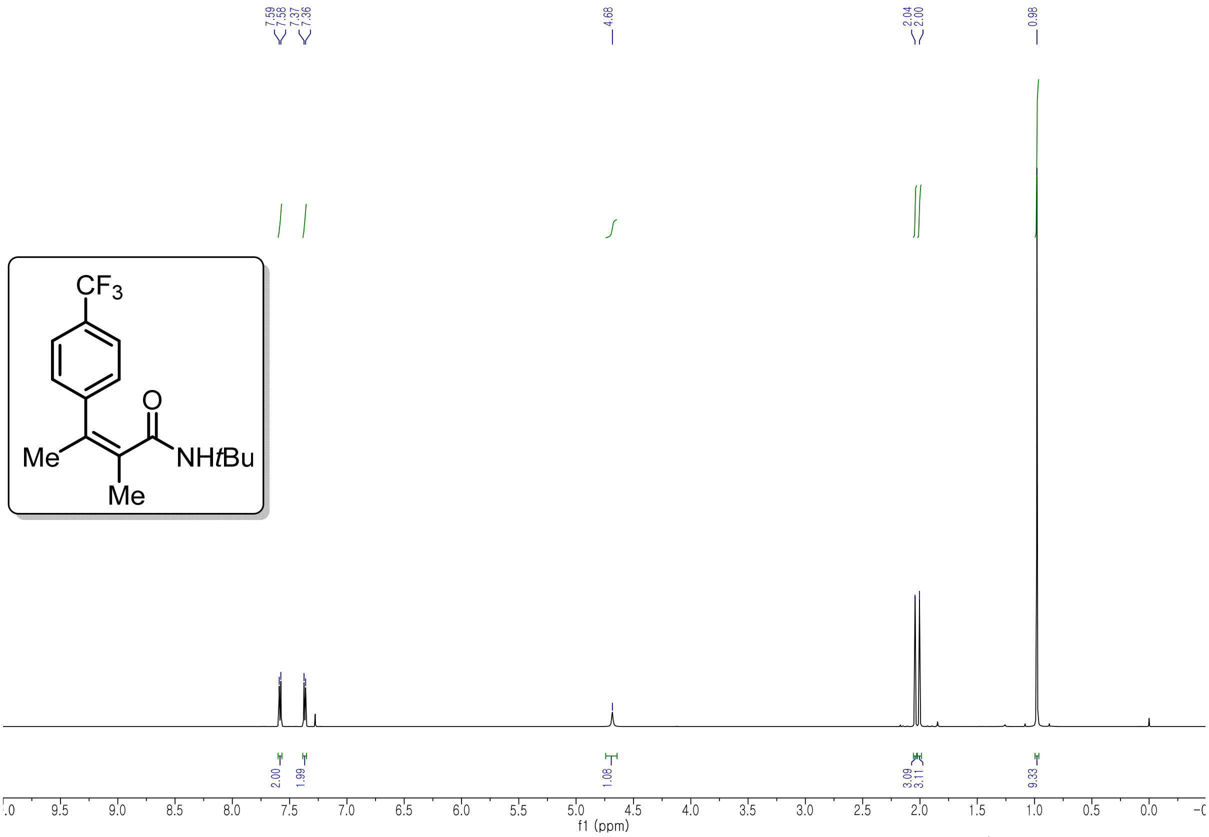
***(Z)*-*N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methylbut-2-enamide** (Table 4, **5c**)

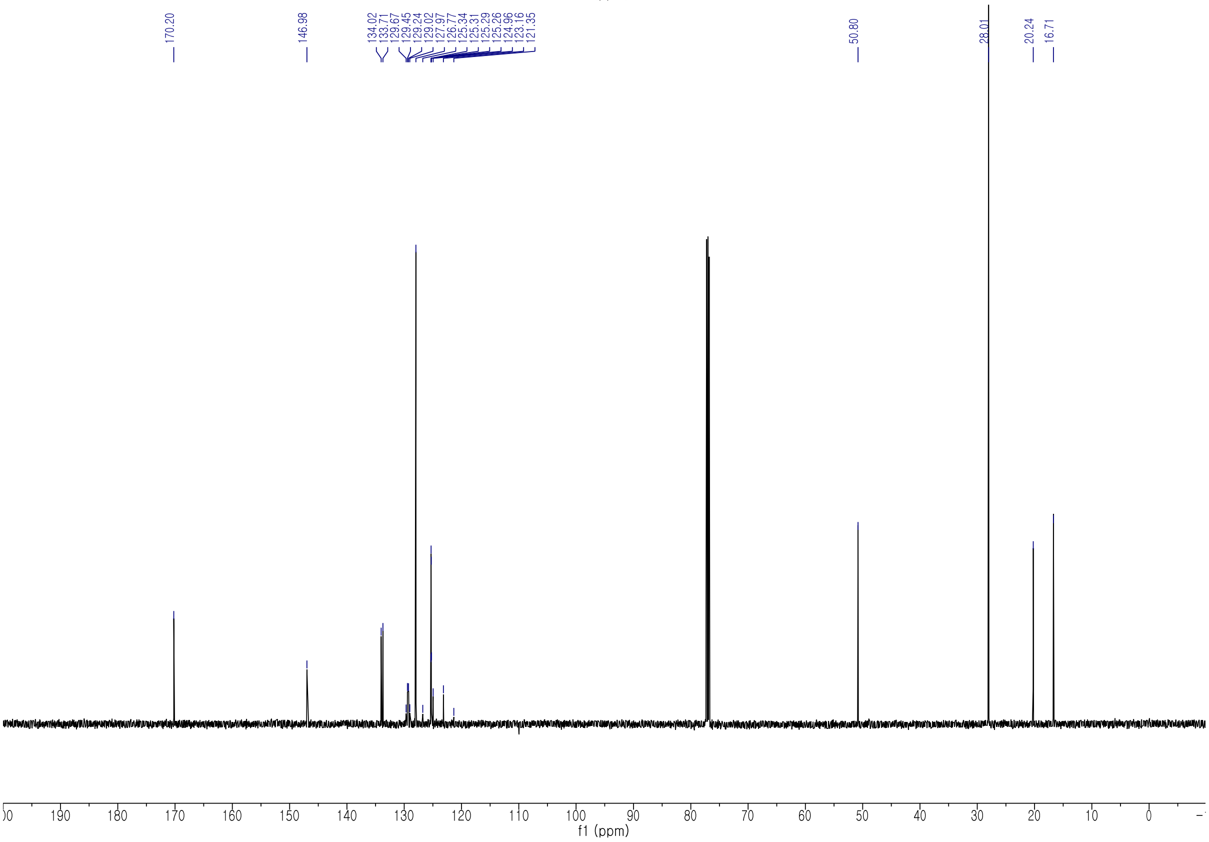


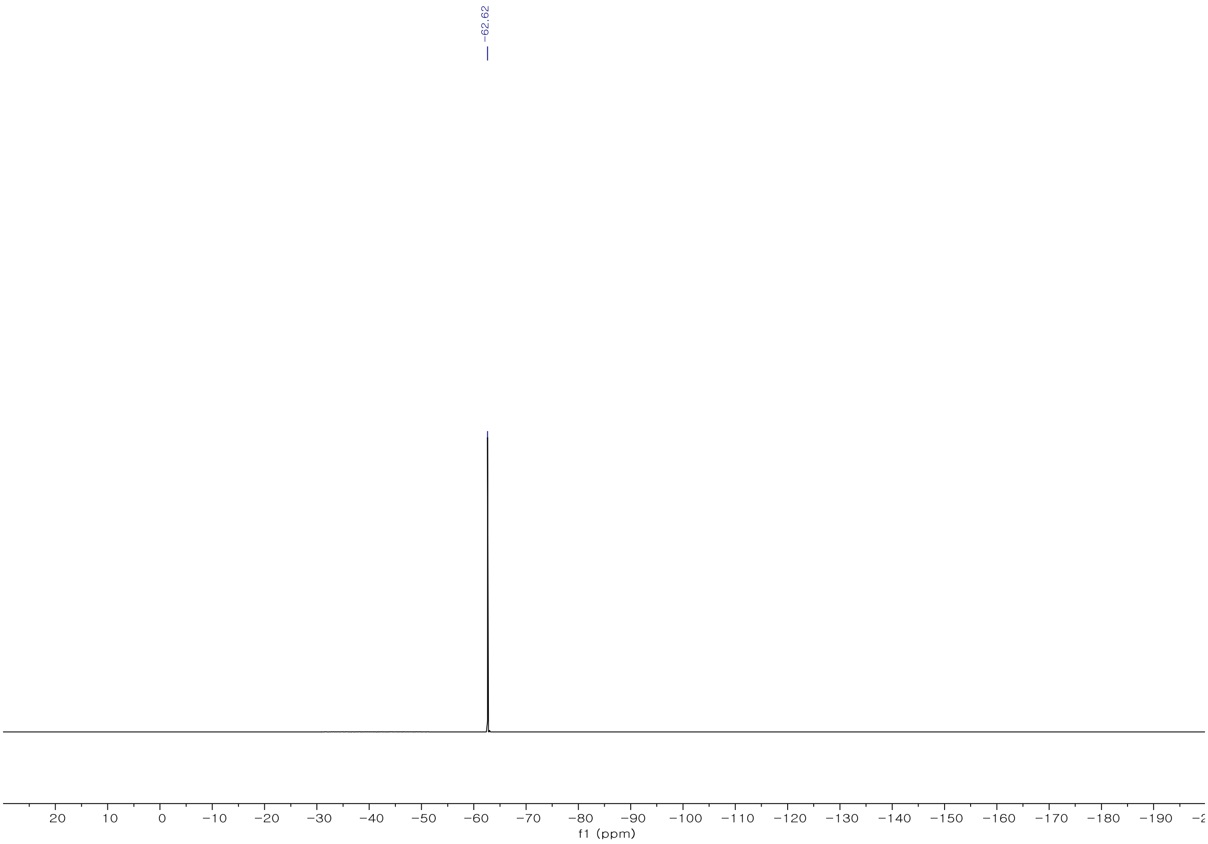




***(Z)-N*-(*tert*-Butyl)-2-methyl-3-[4-(trifluoromethyl)phenyl]but-2-enamide** (Table 4, **5d**)

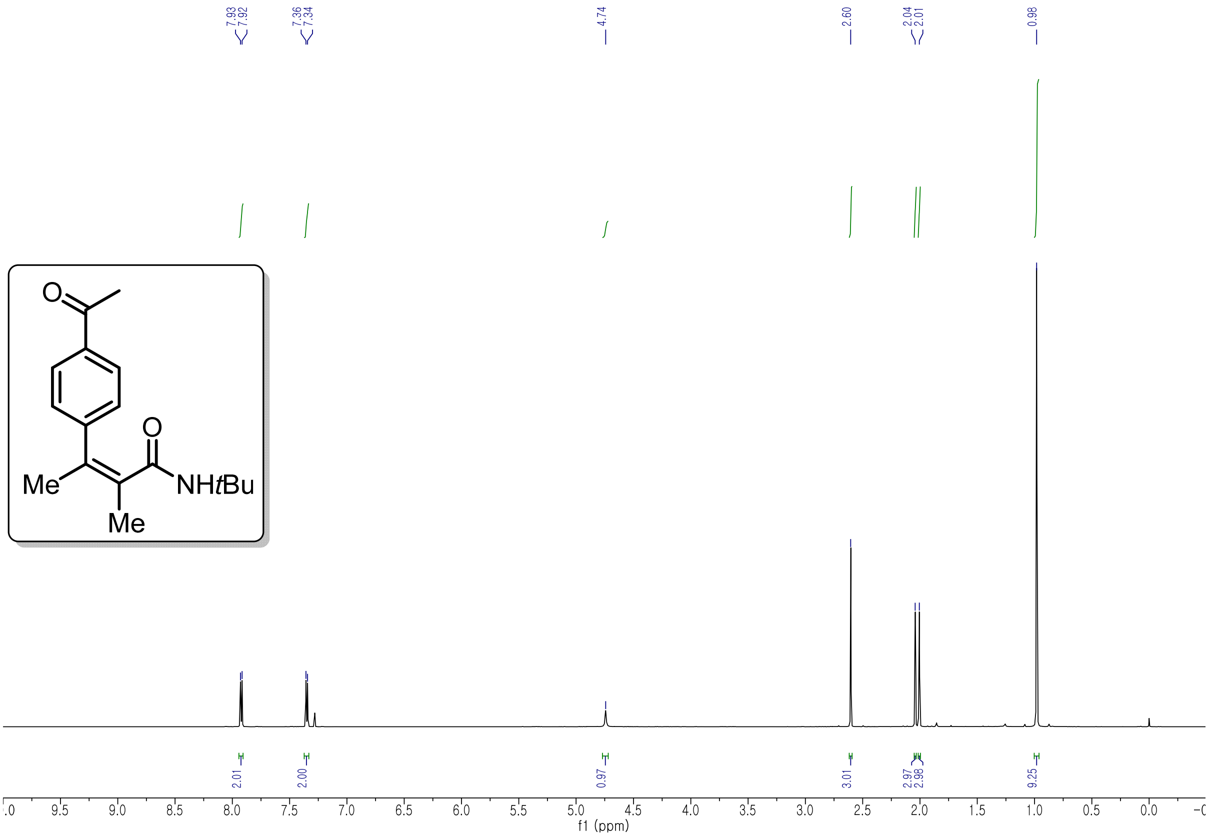


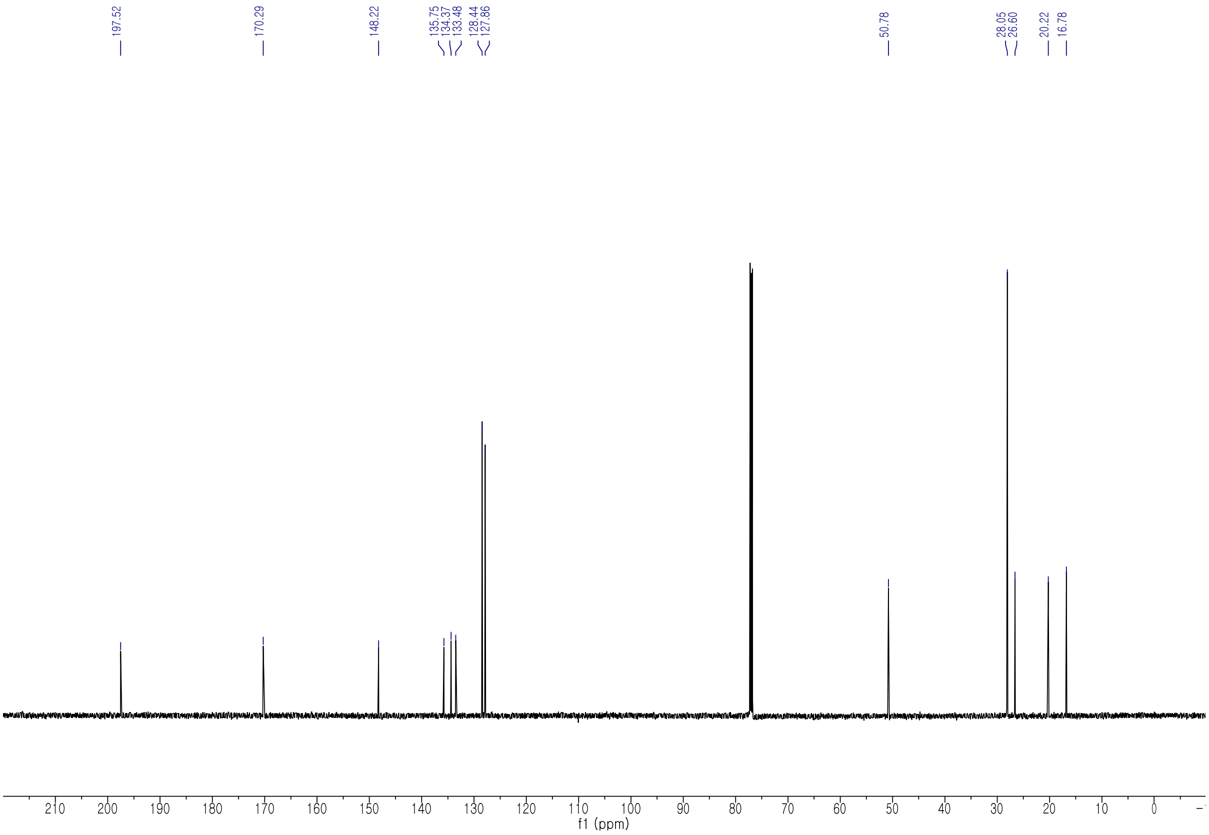




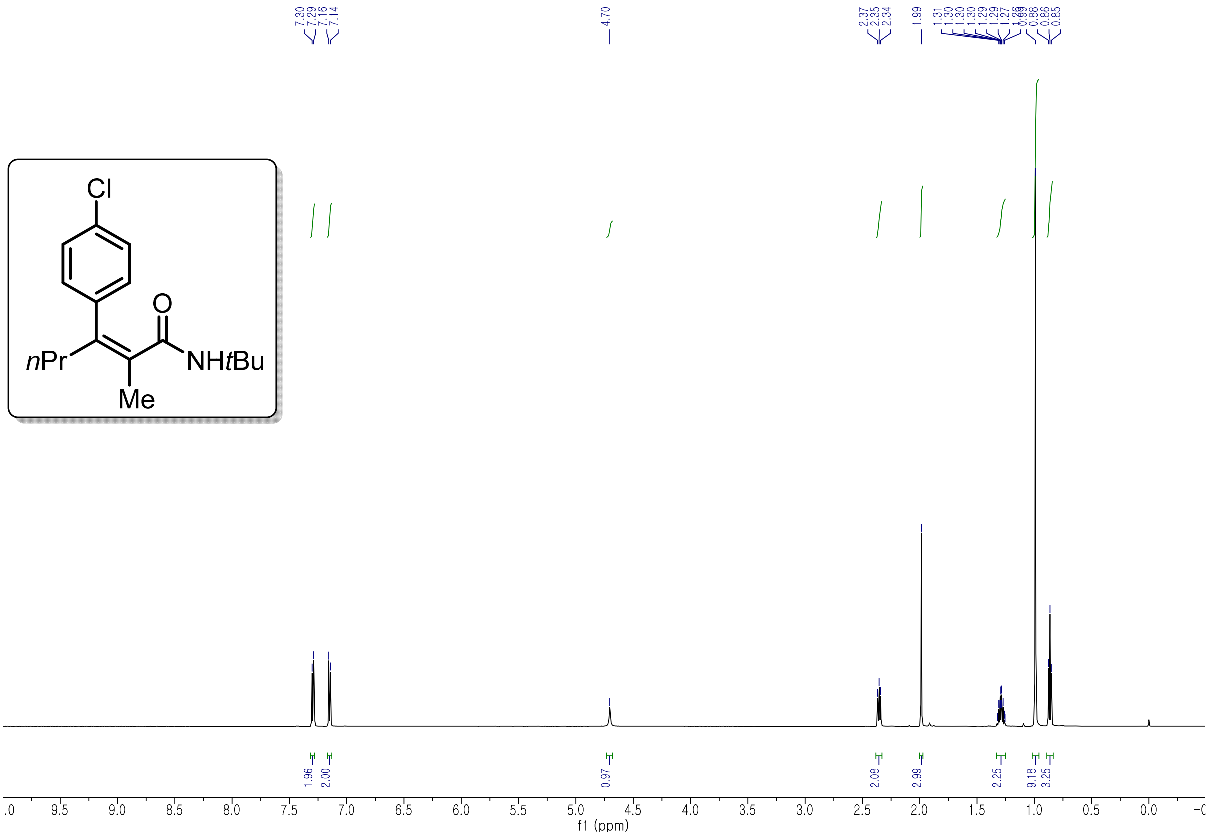
−62.62
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

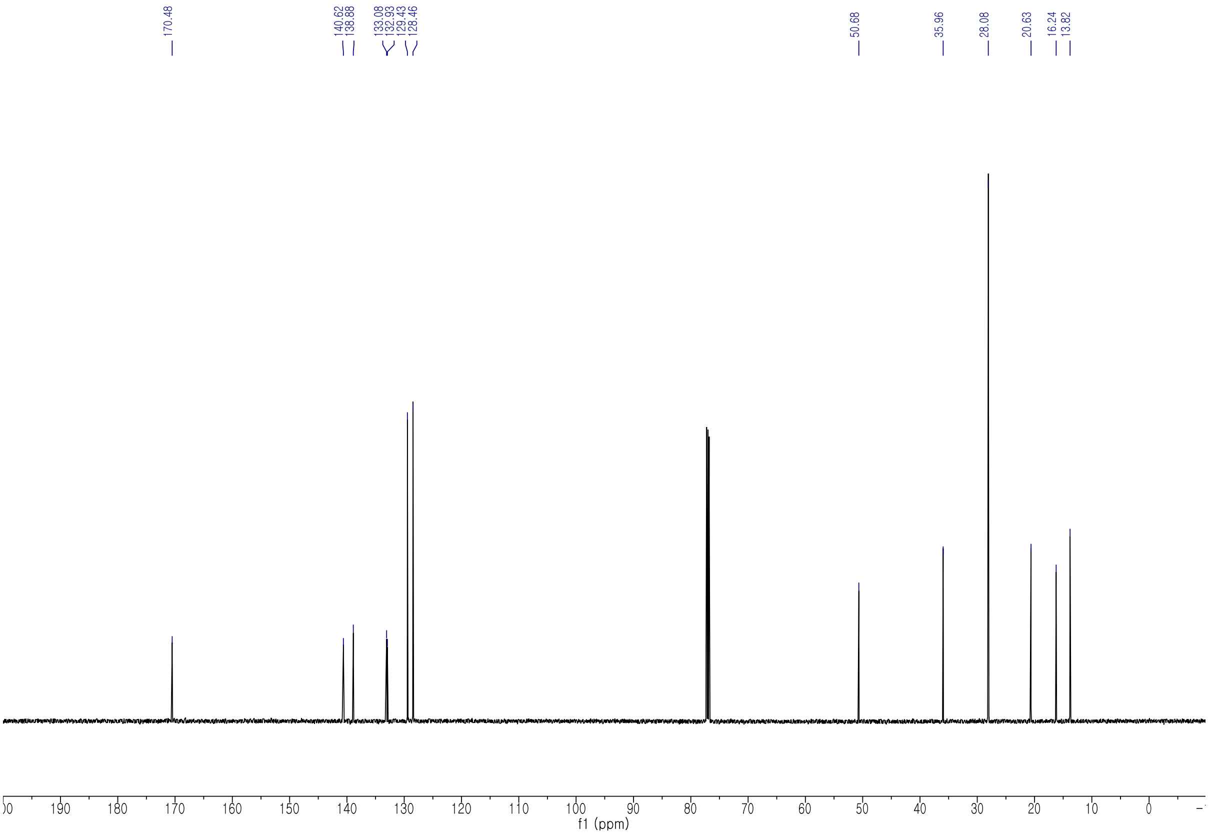
(Z)-N-(tert-**Butyl)-3-(4-acetylphenyl)-2-methylbut-2-enamide** (Table 4, **5e**)



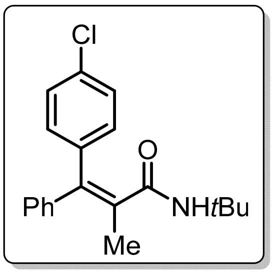


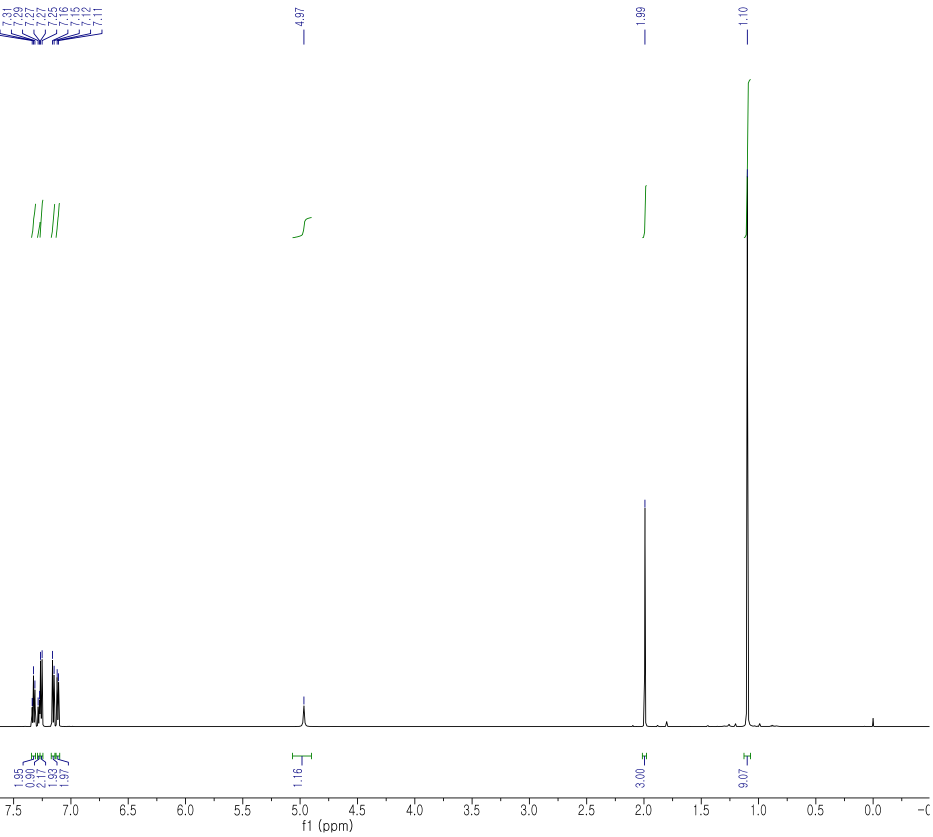
***(Z)-N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methylhex-2-enamide** (Table 4, **5f**)

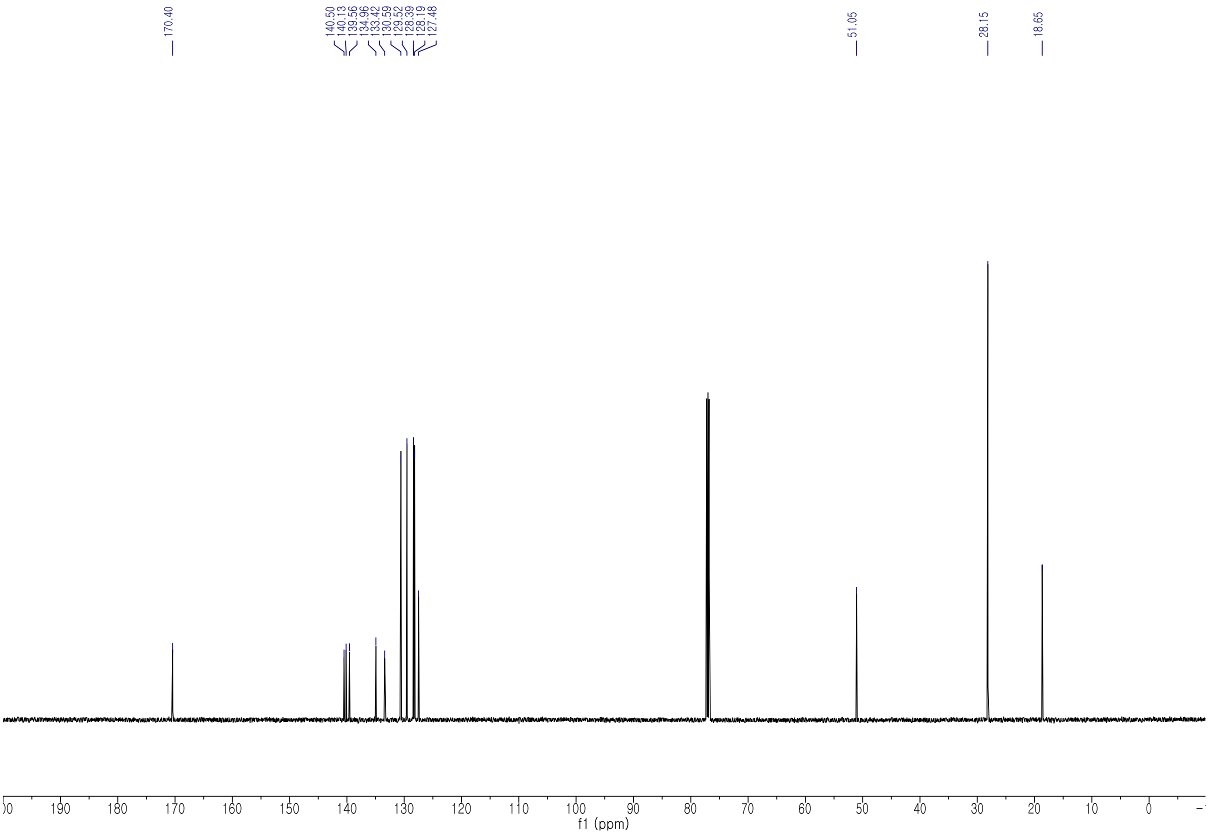




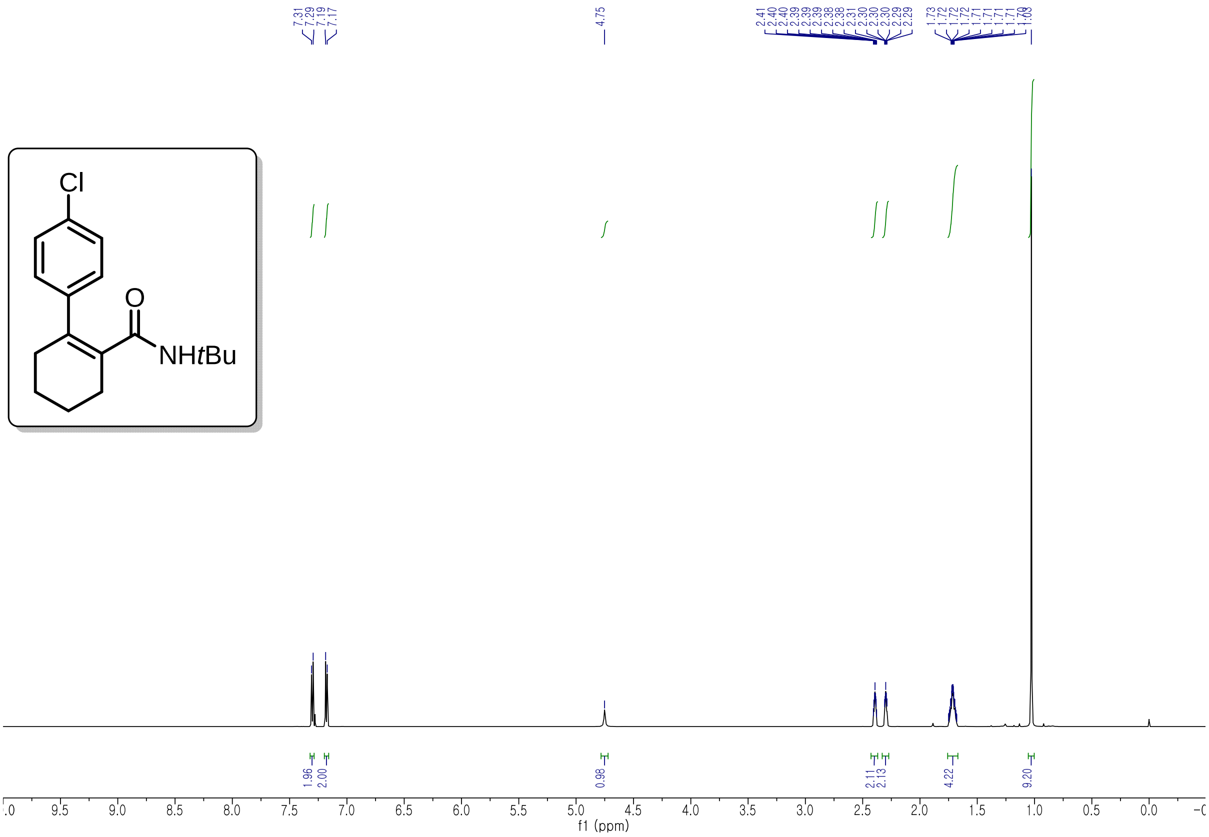
***(Z)*-*N*-(*tert*-Butyl)-3-(4-chlorophenyl)-2-methyl-3-phenylacrylamide** (Table 4, **5g**)

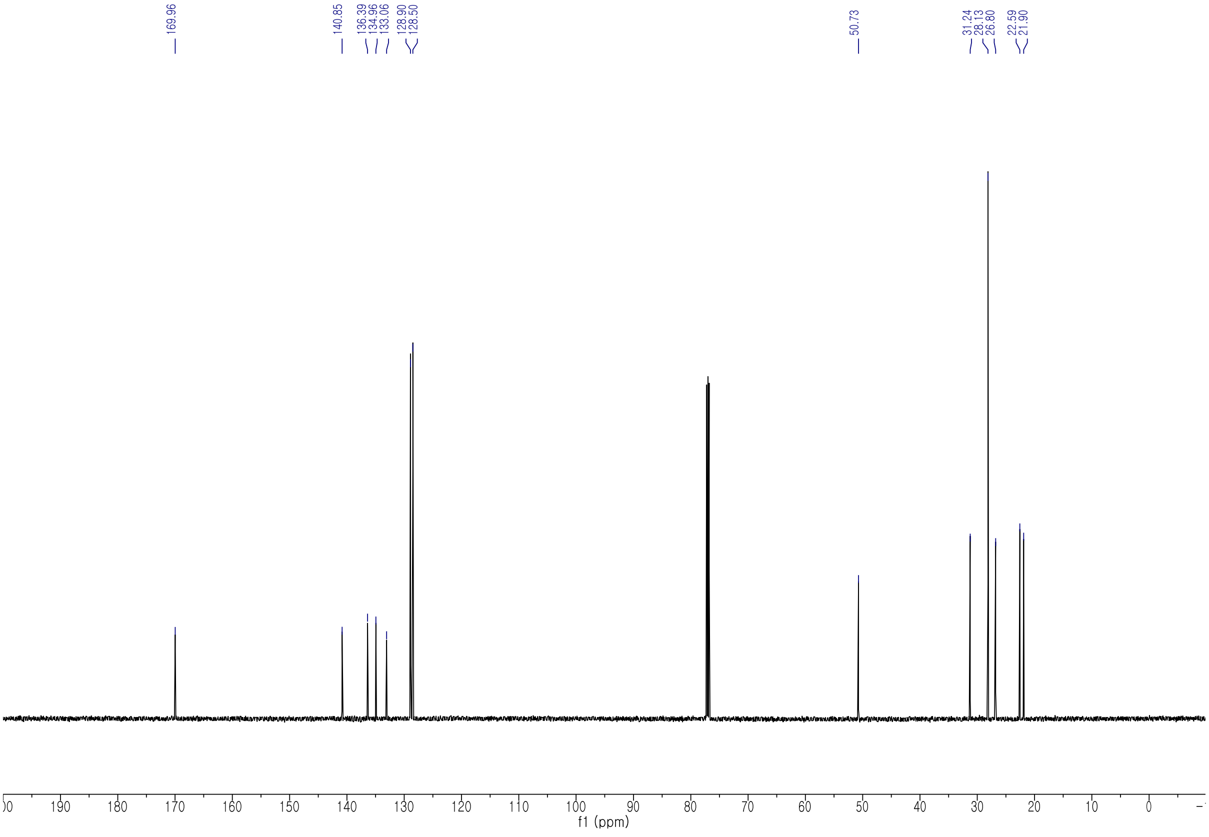




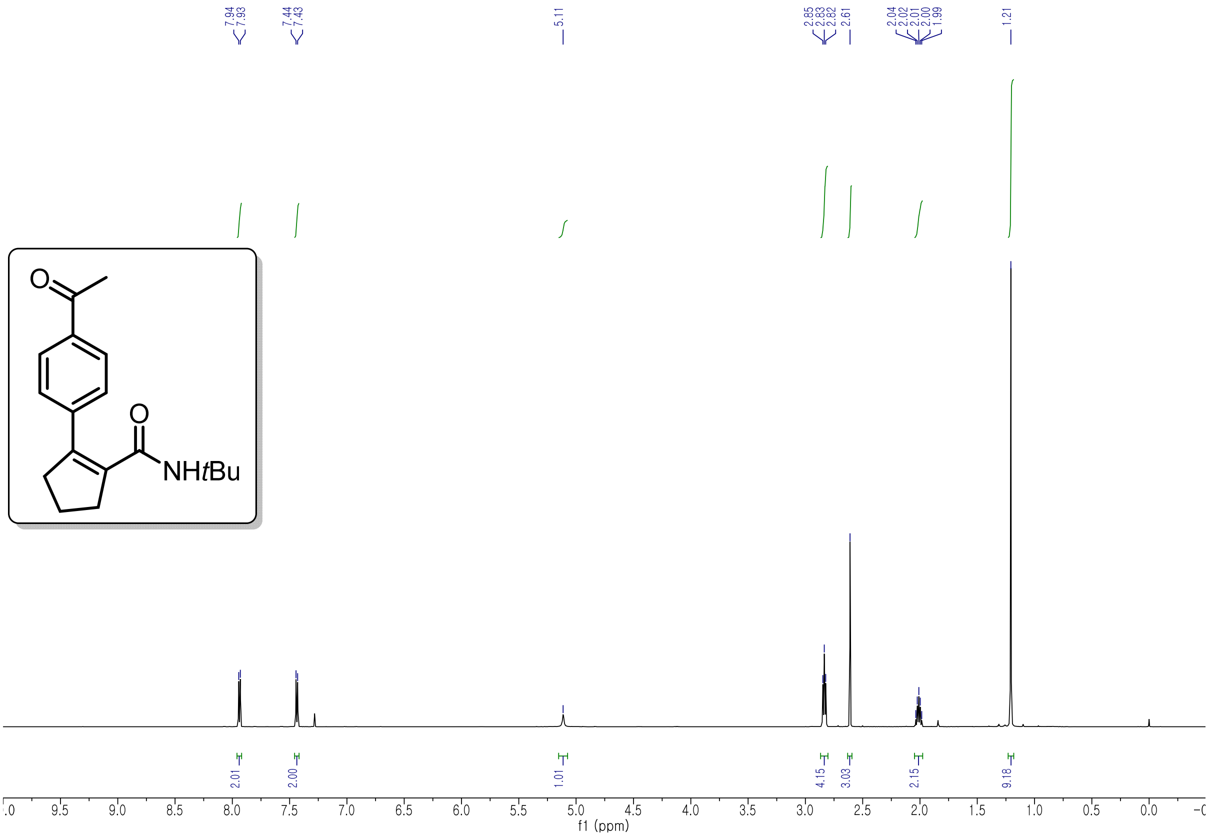


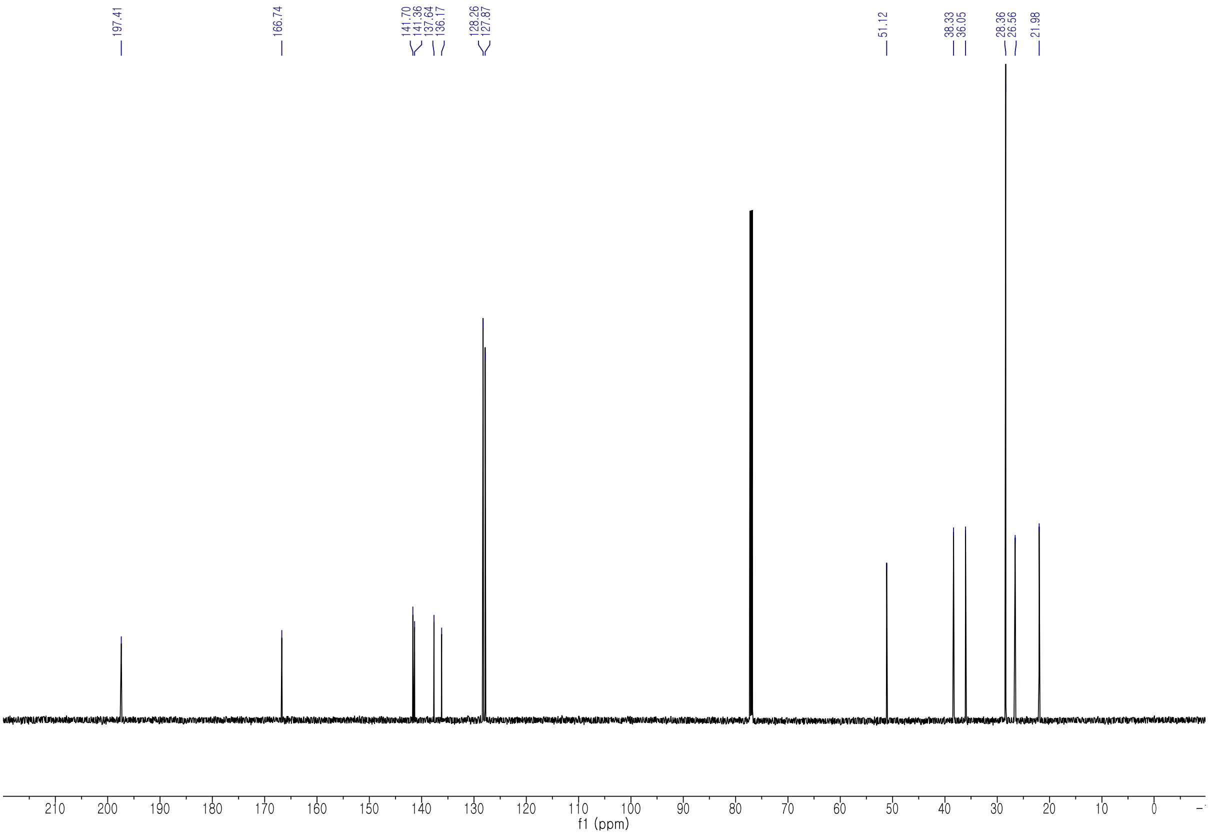
***N*-(*tert*-Butyl)-2-(4-chlorophenyl)cyclohex-1-ene-1-carboxamide** (Table 4, **5h**)



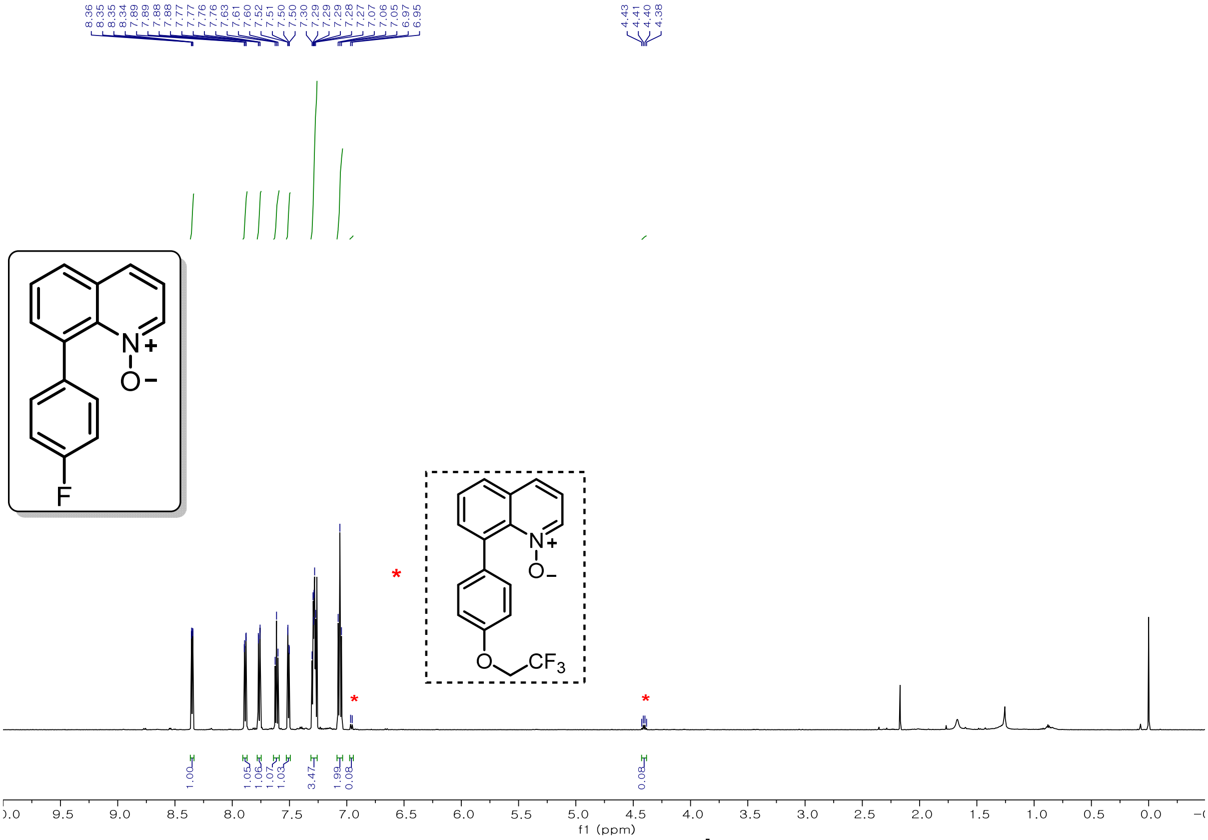


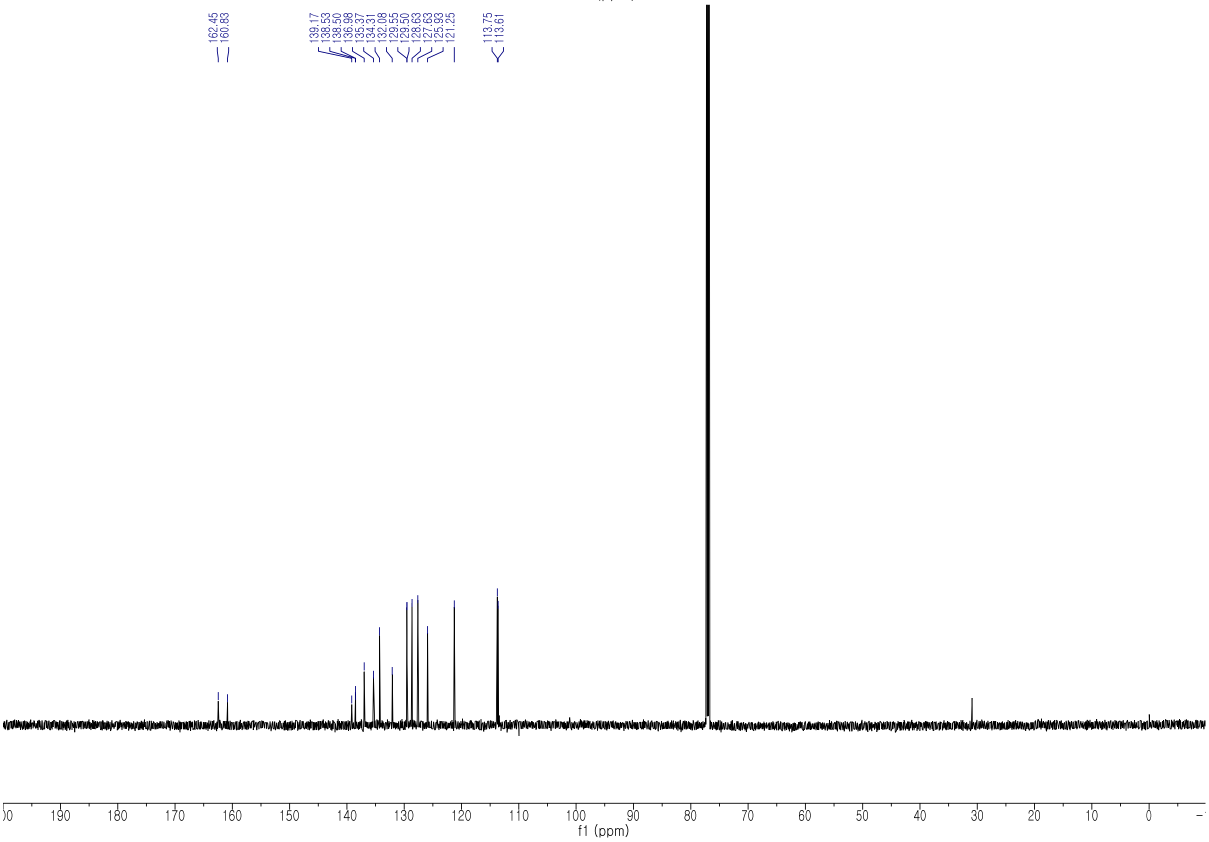
***N*-(*tert*-Butyl)-2-(4-acetylphenyl)cyclopent-1-ene-1-carboxamide** (Table 4, **5i**)

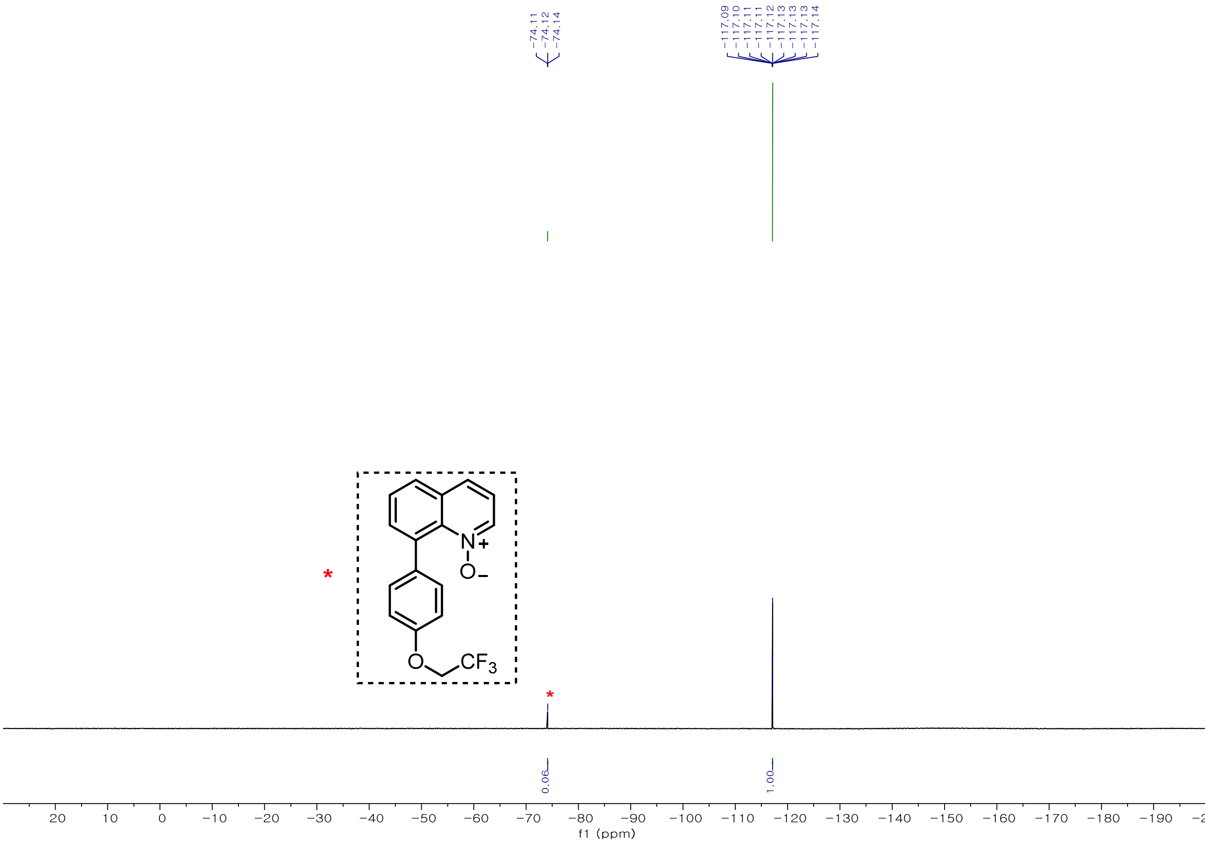




8-(4-Fluorophenyl)quinoline 1-oxide (Table 5, **7a**)

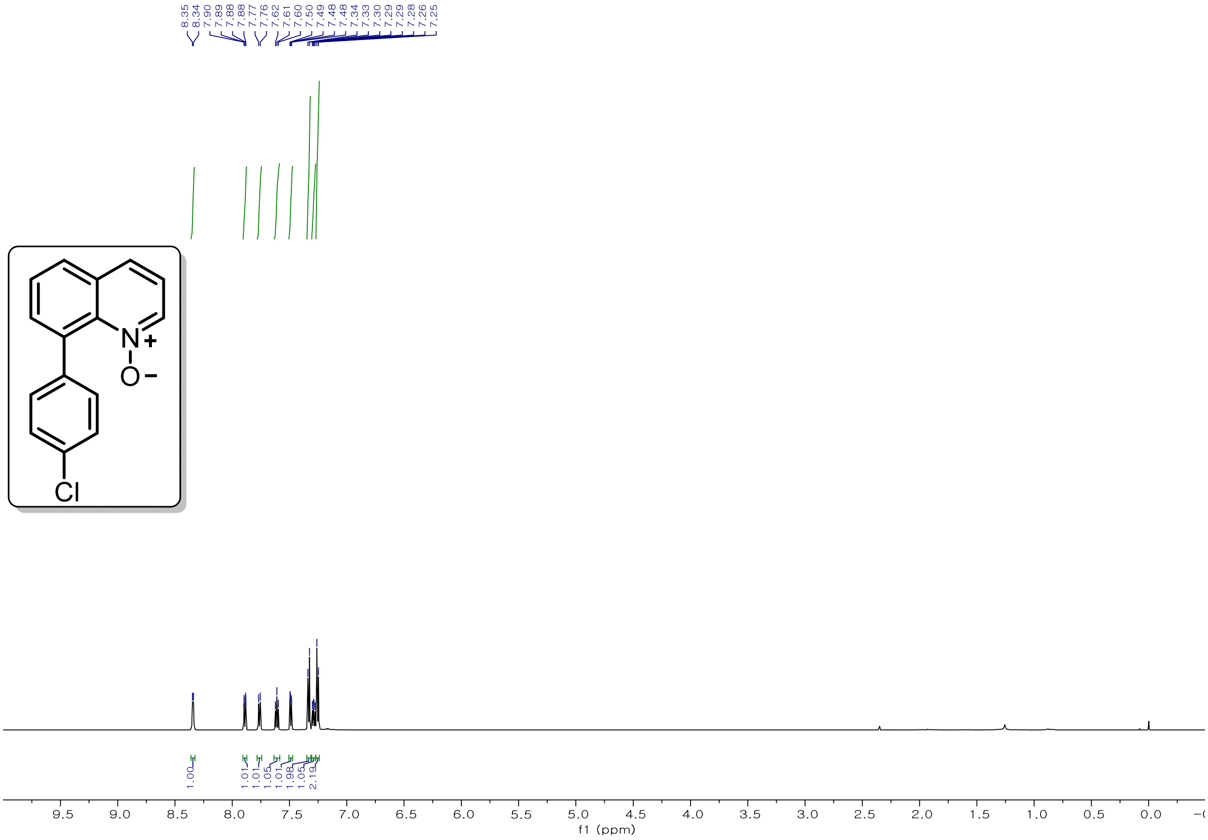


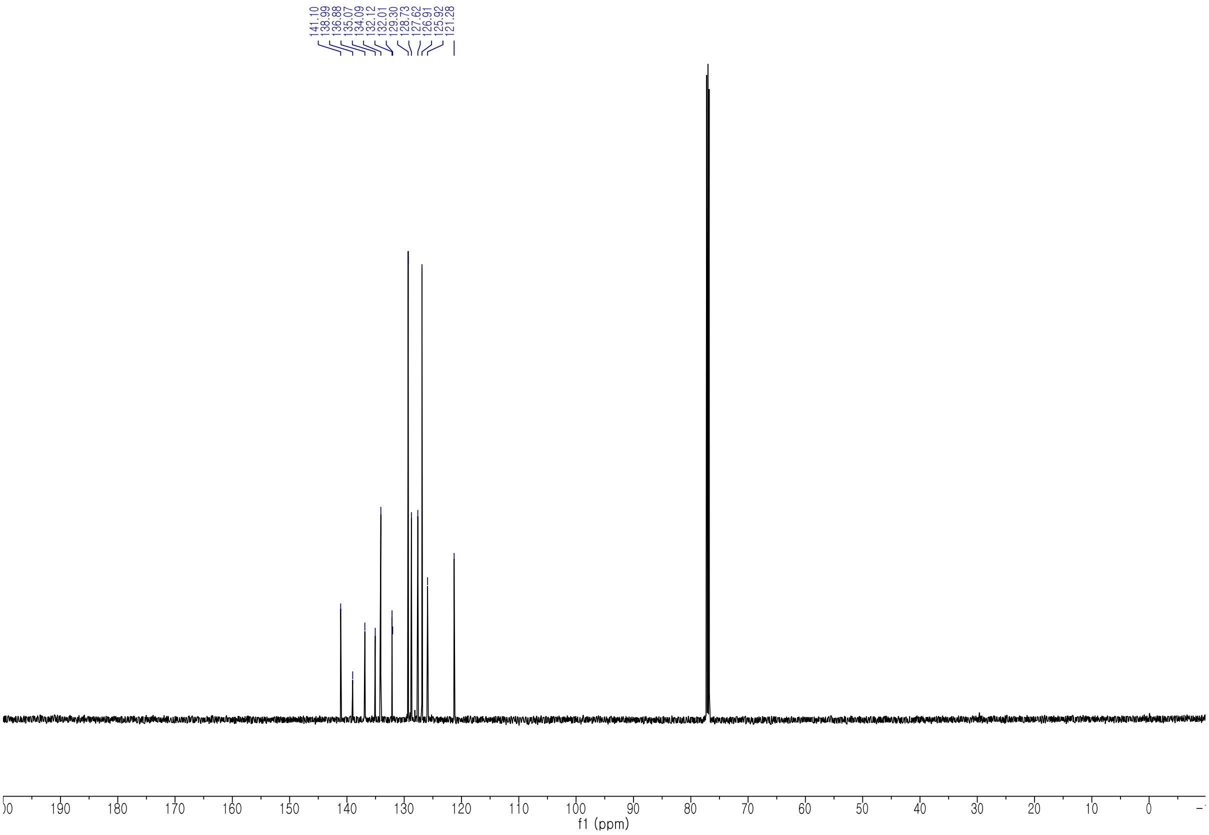




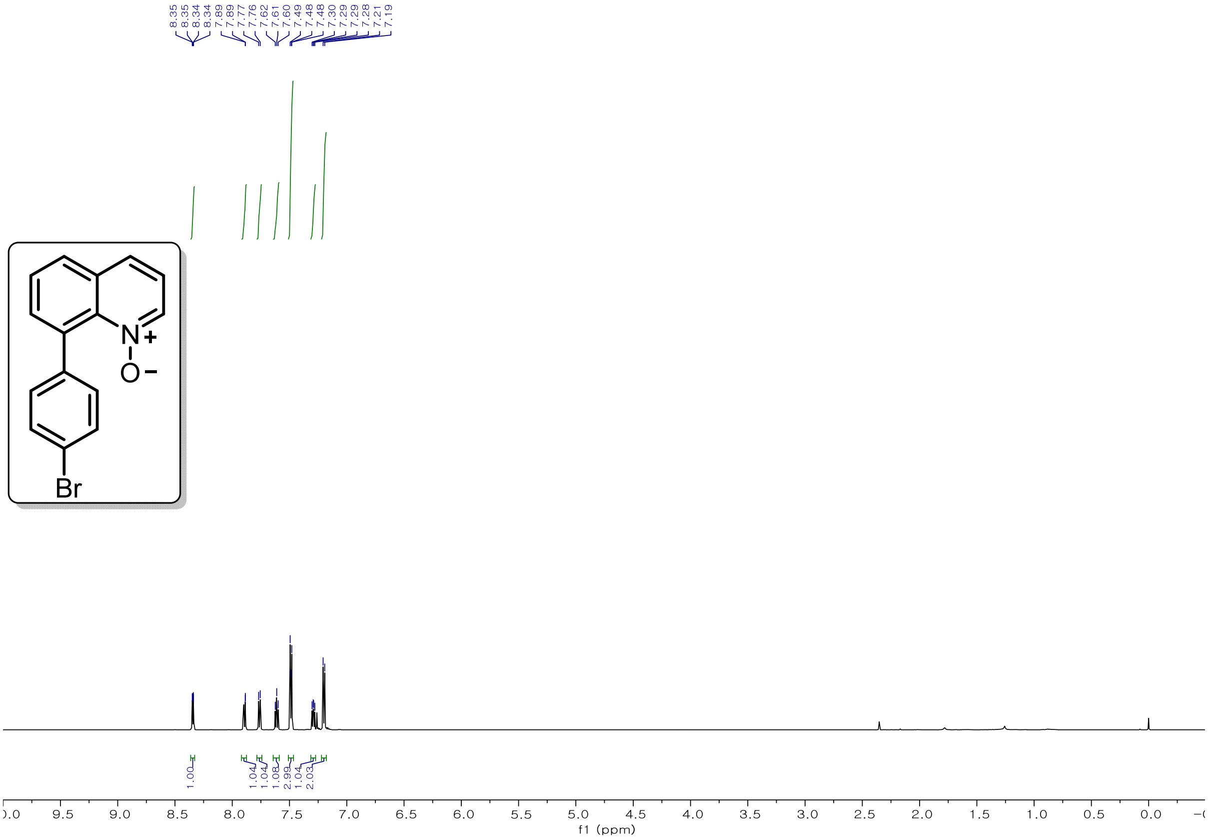
-74.11
-74.12
-74.14
-117.09
-117.10
-117.11
-117.11
-117.12
-117.13
-117.13
-117.13
-117.14
N+
O−
O
CF3
*
*
0.06
1.00
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

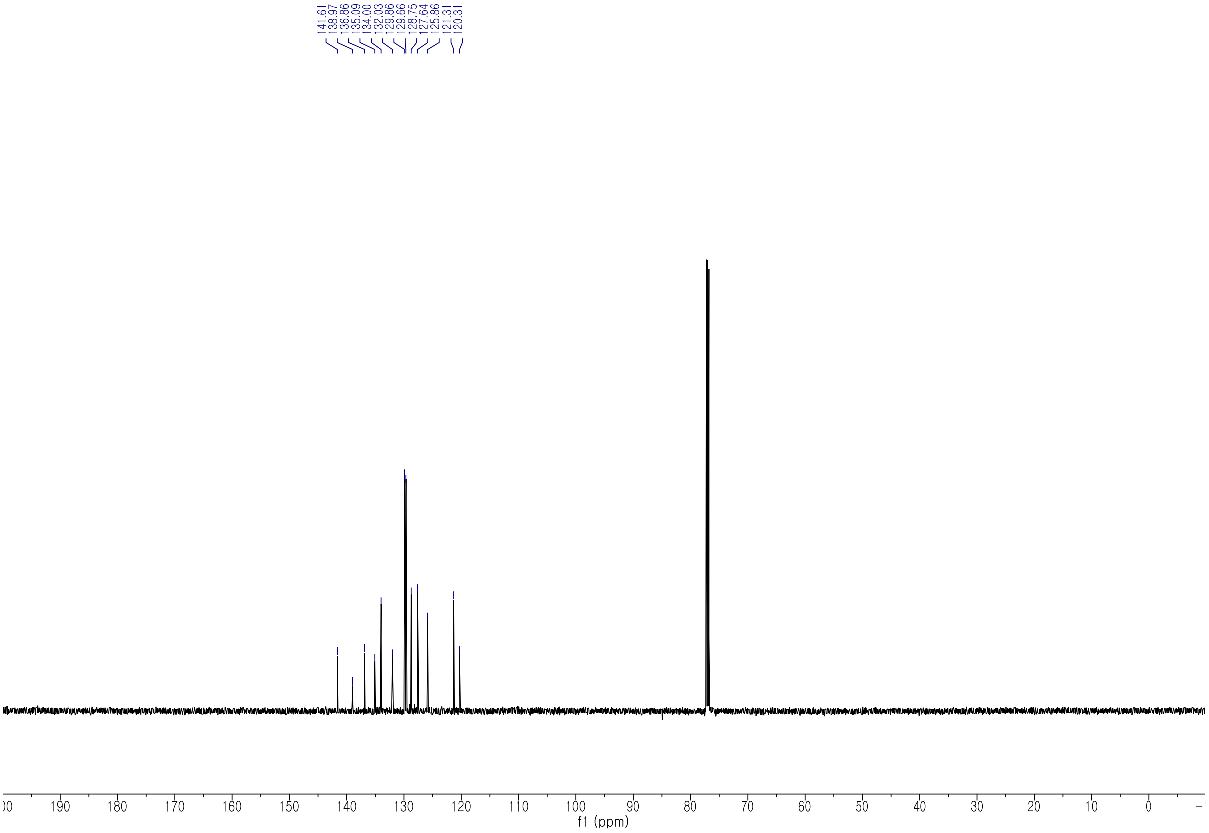
8-(4-Chlorophenyl)quinoline 1-oxide (Table 5, **7b**)



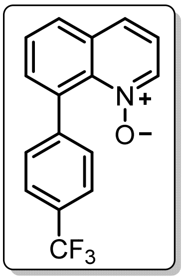


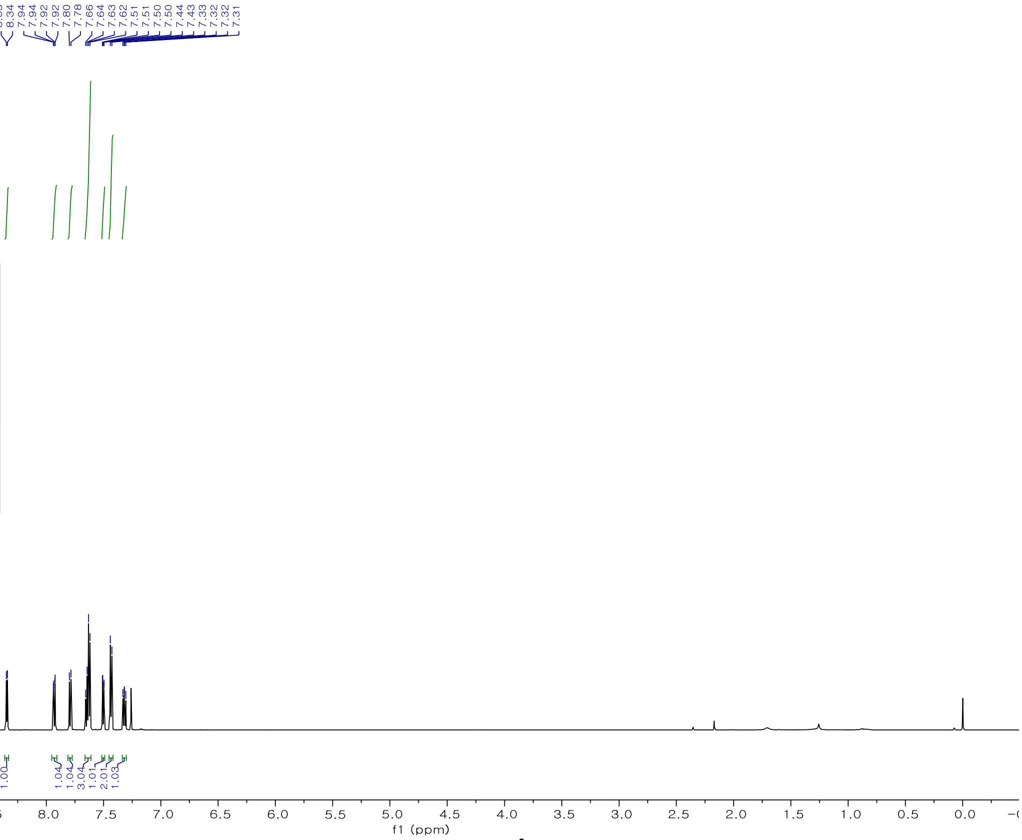
8-(4-Bromophenyl)quinoline 1-oxide (Table 5, **7c**)

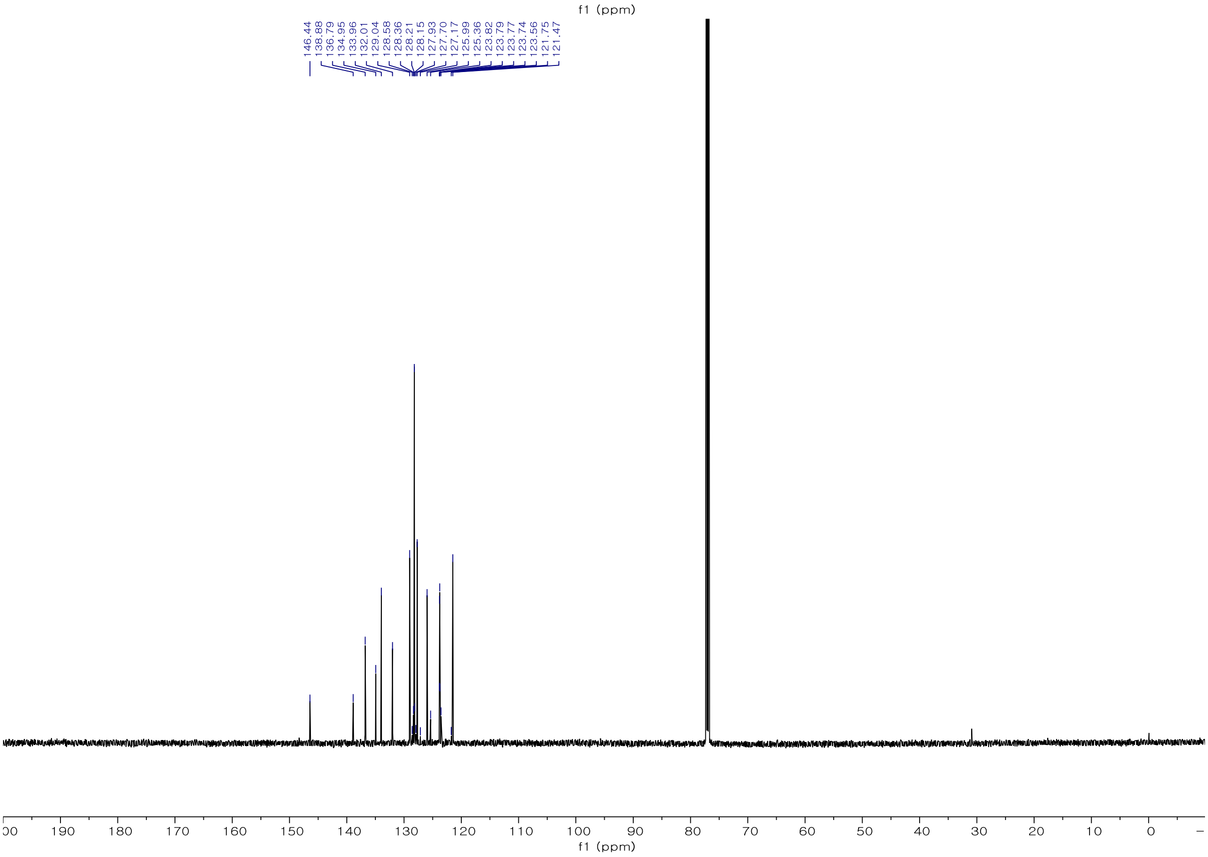


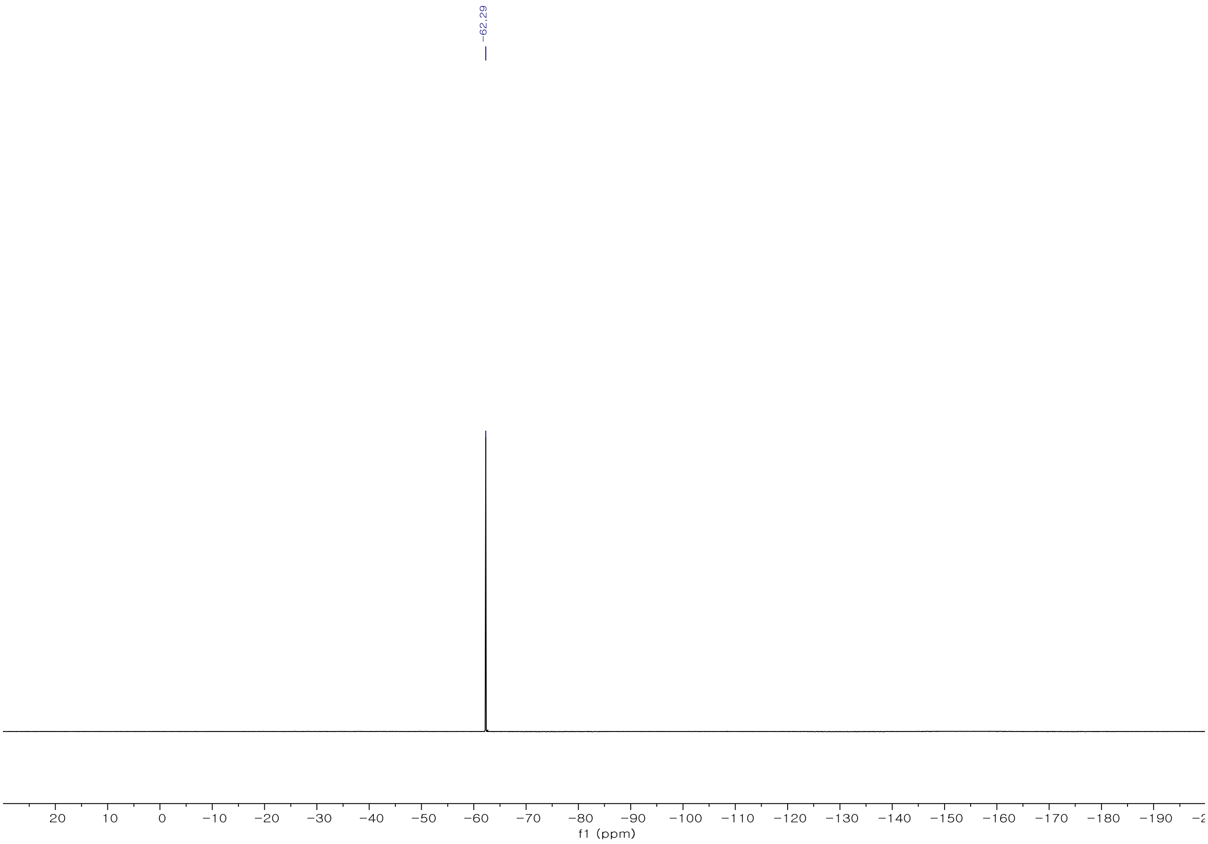


8-[4-(Trifluoromethyl)]quinoline 1-oxide (Table 5, **7d**)



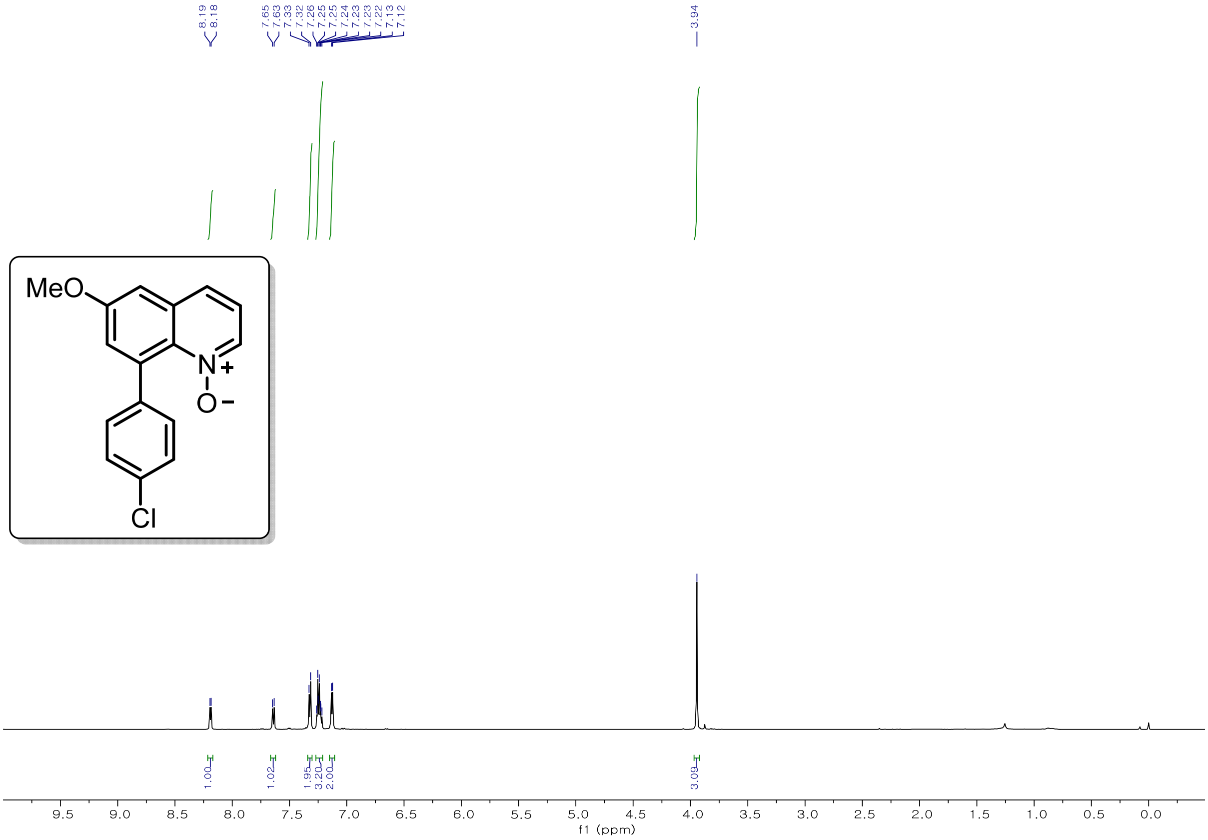


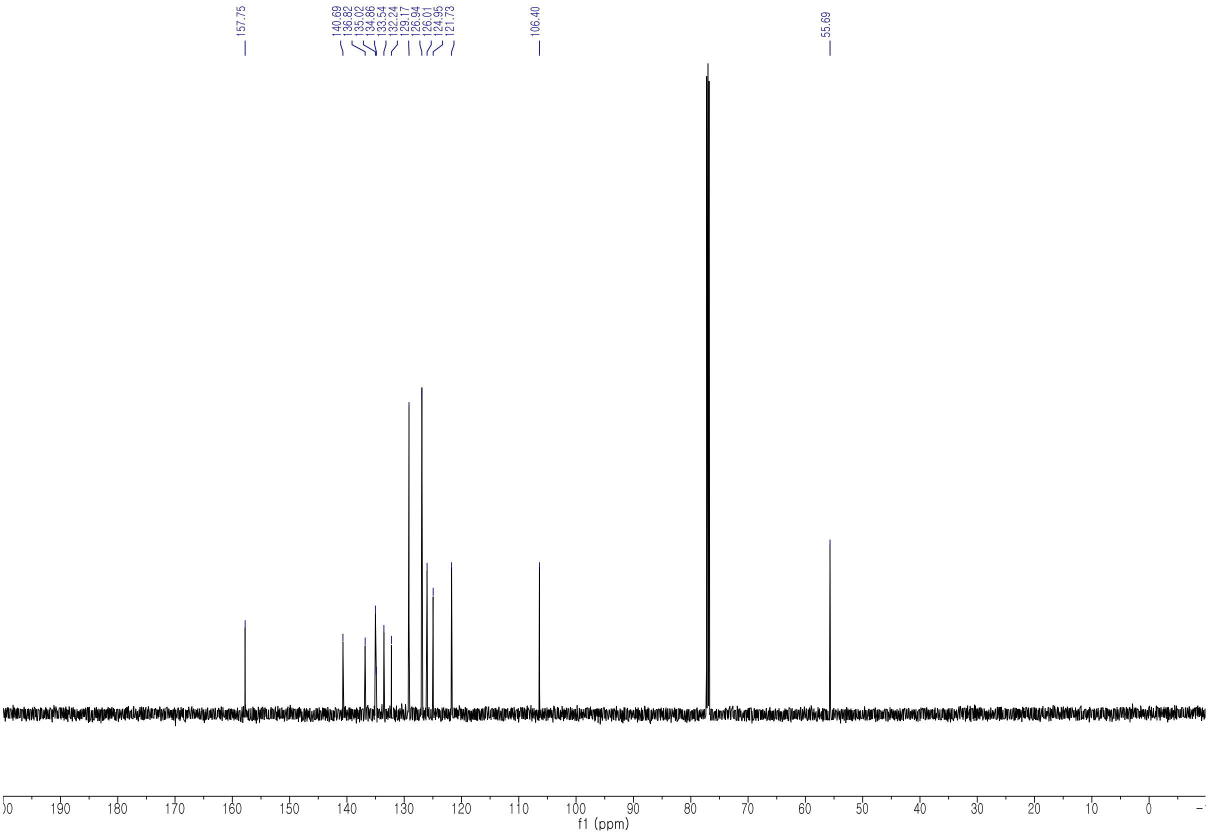




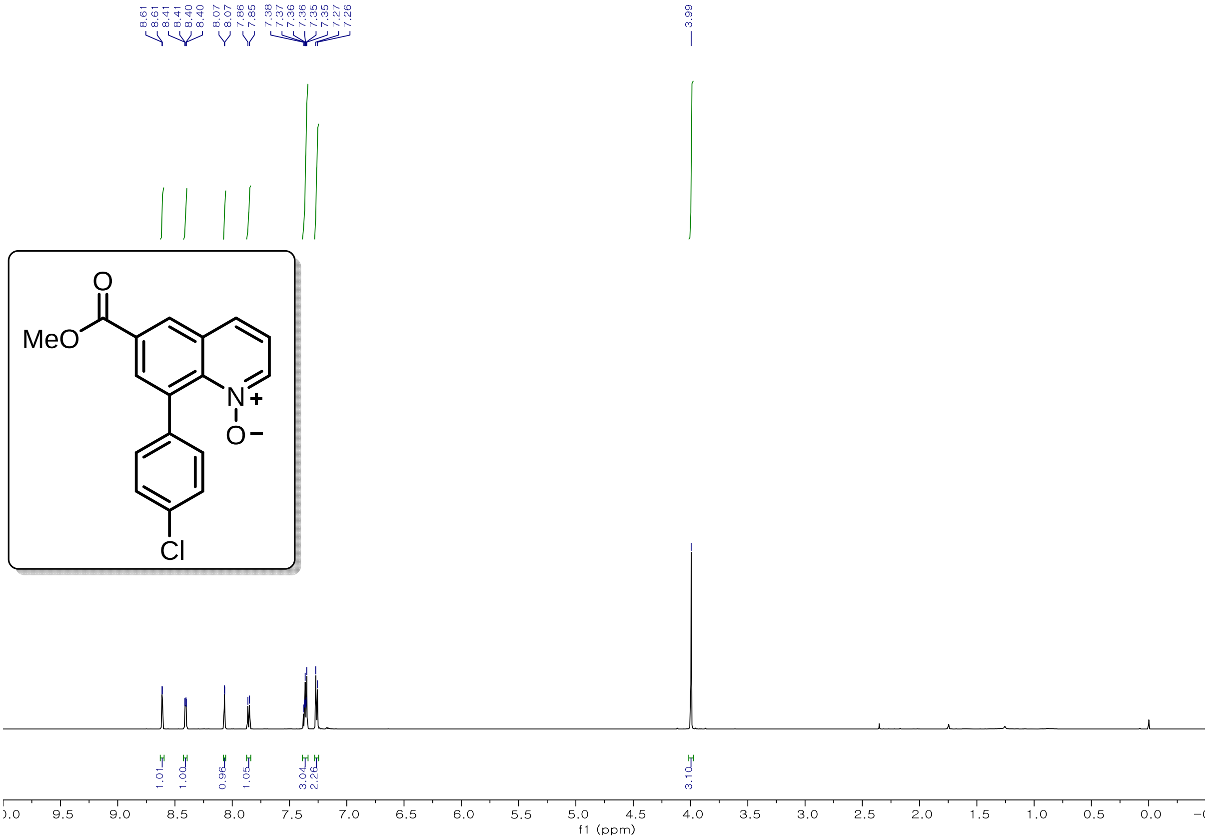
-62.29
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

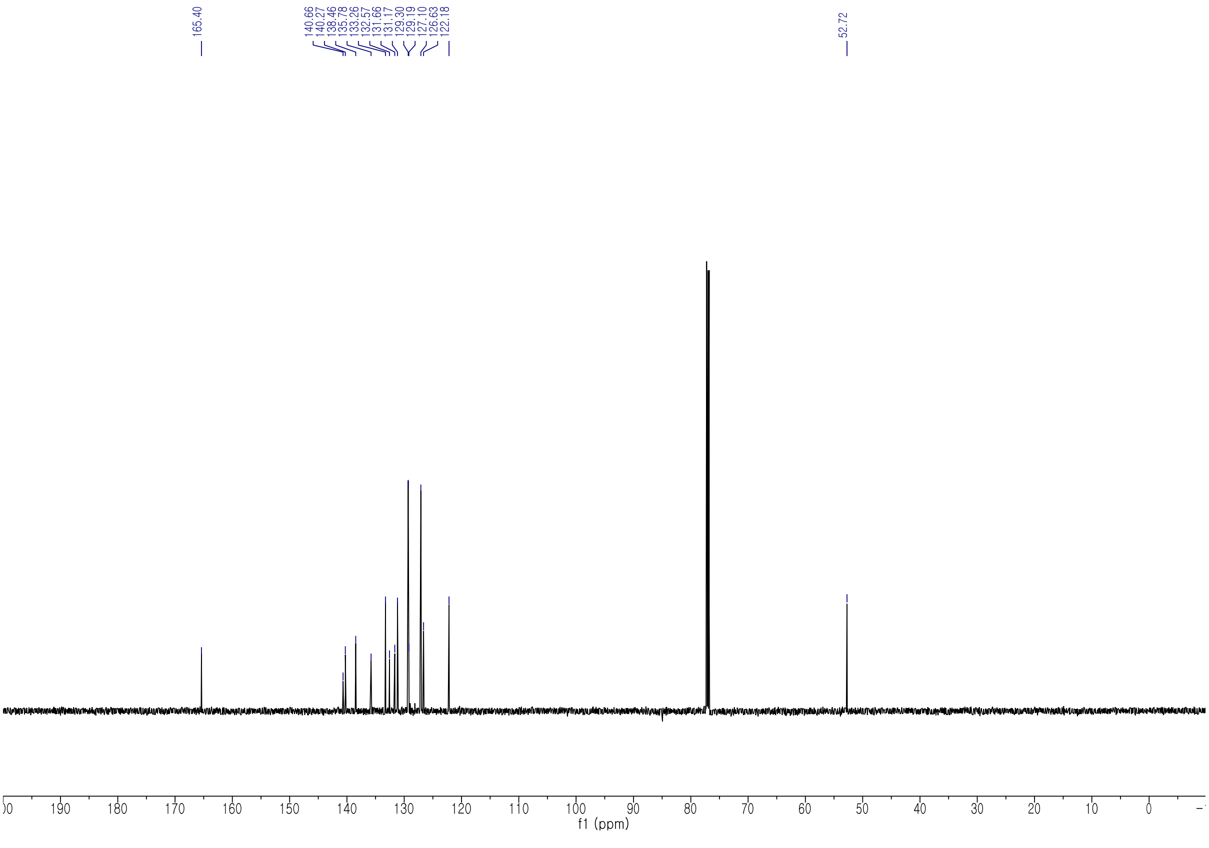
8-(4-Chlorophenyl)-6-methoxyquinoline 1-oxide (Table 5, **7e**)



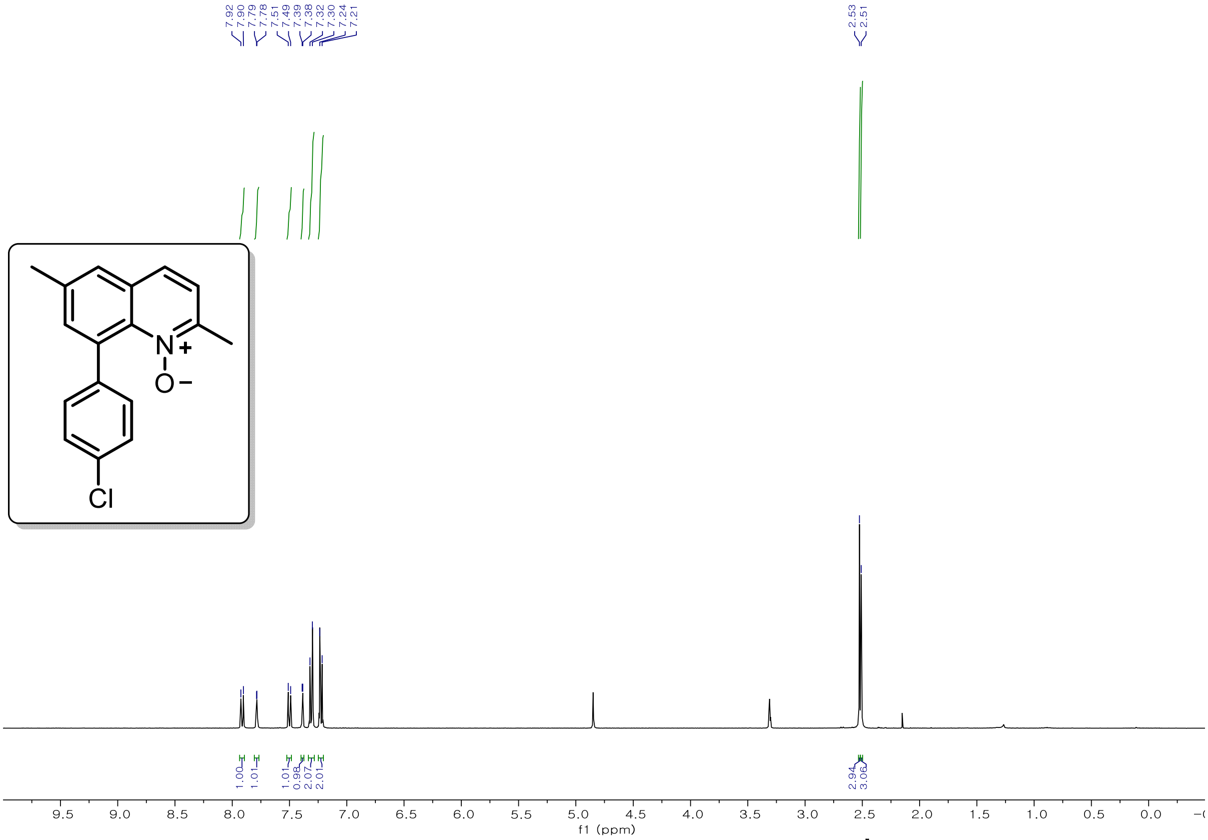


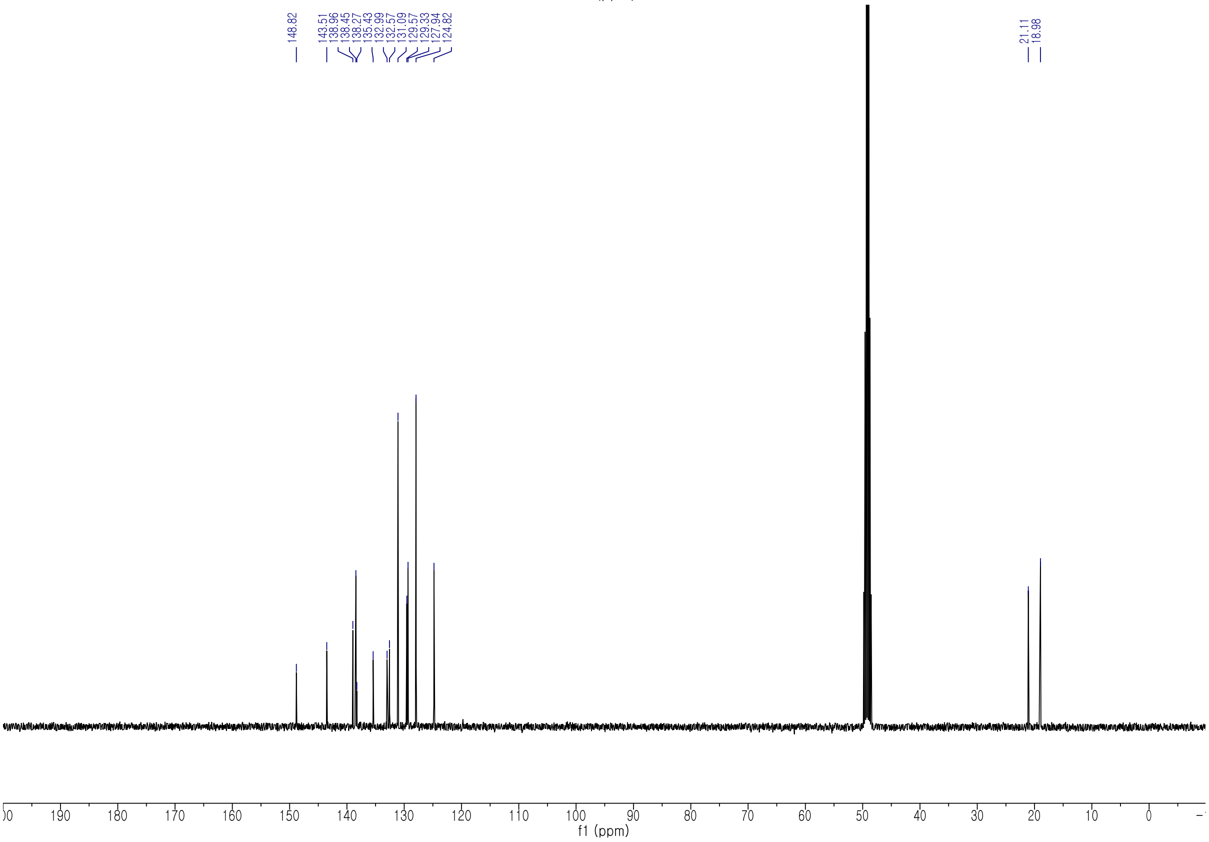
8-(4-Chlorophenyl)-6-methoxycarbonylquinoline 1-oxide (Table 5, **7f**)



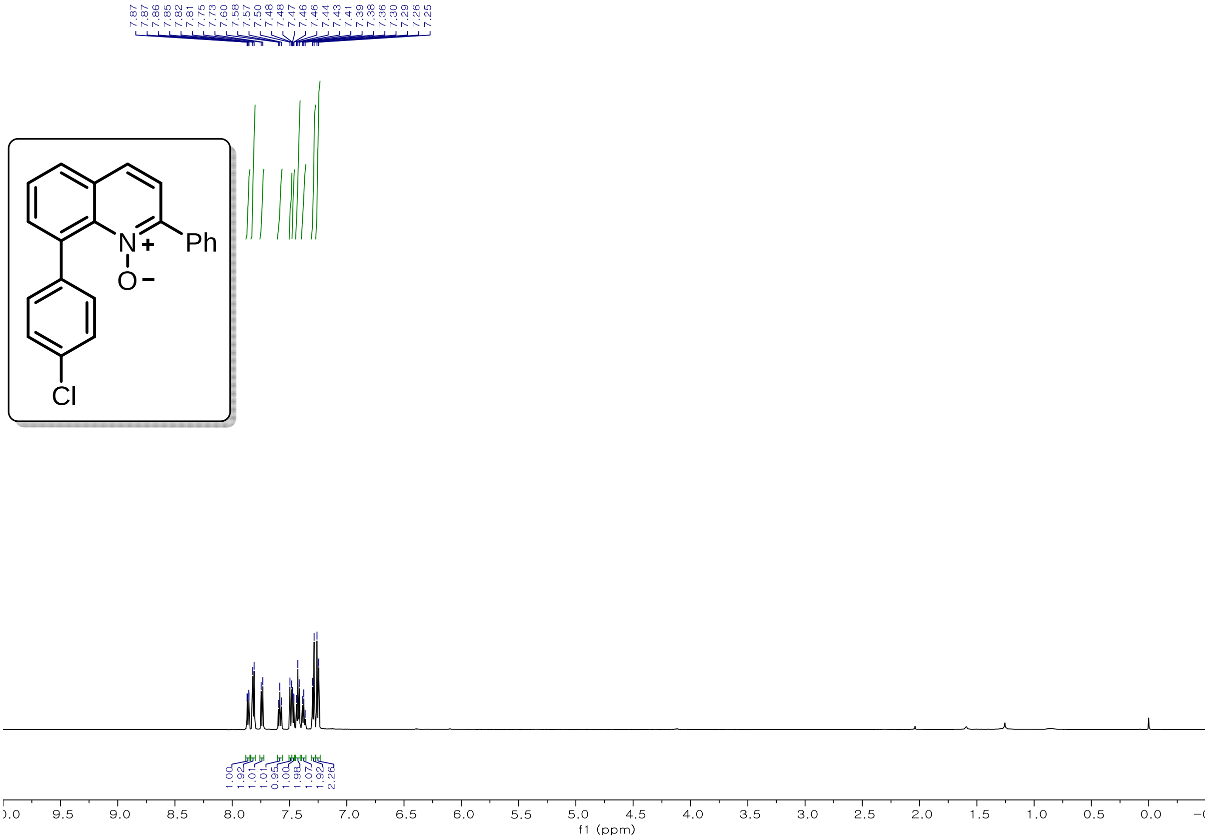


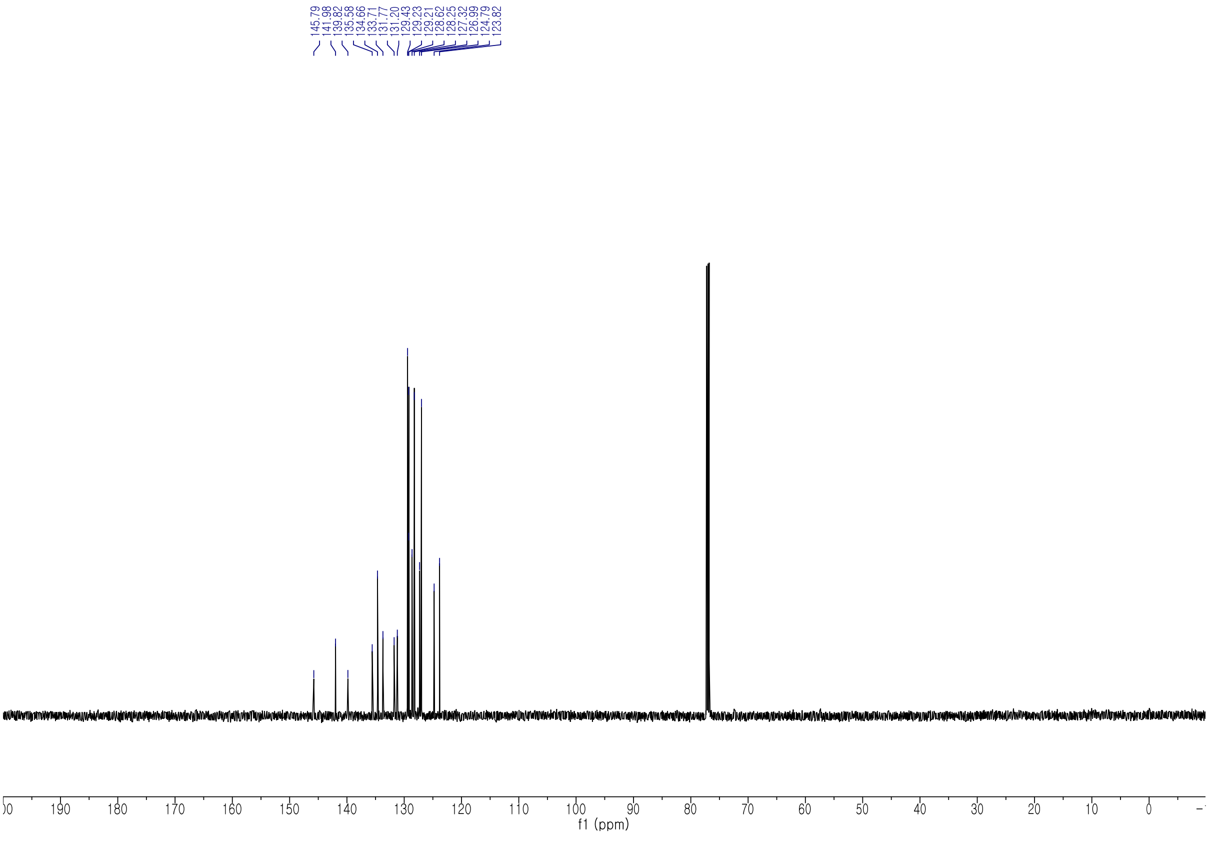
8-(4-Chlorophenyl)-2,6-dimethylquinoline 1-oxide (Table 5, **7g**)



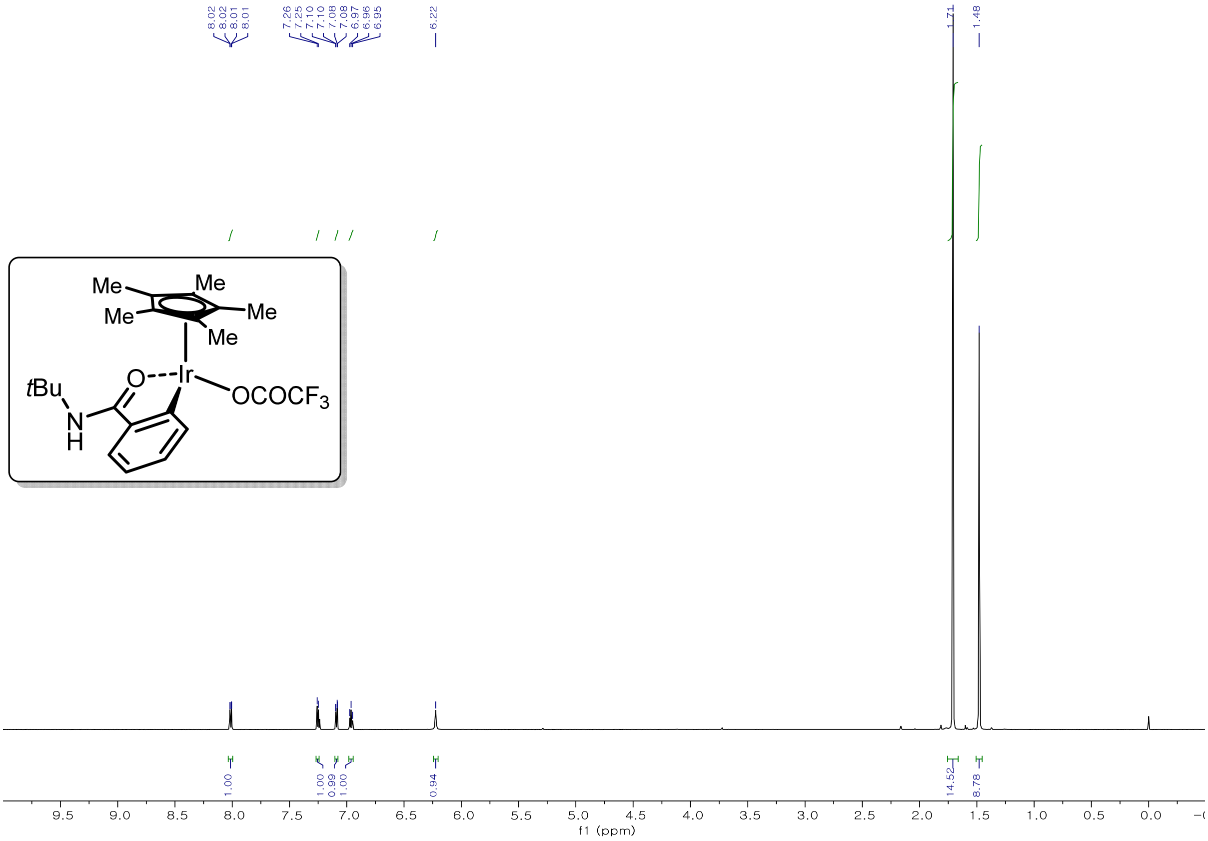


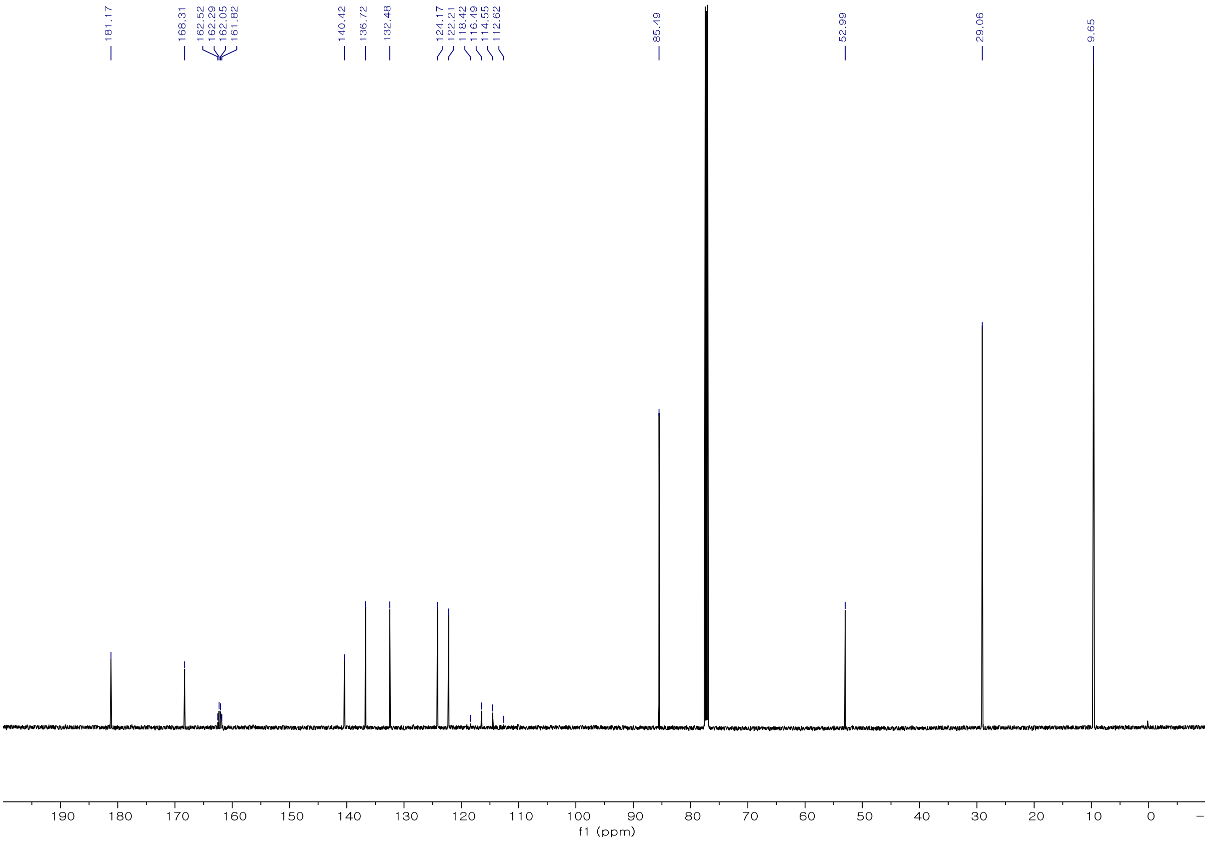
8-(4-Chlorophenyl)-2-phenylquinoline 1-oxide (Table 5, **7h**)

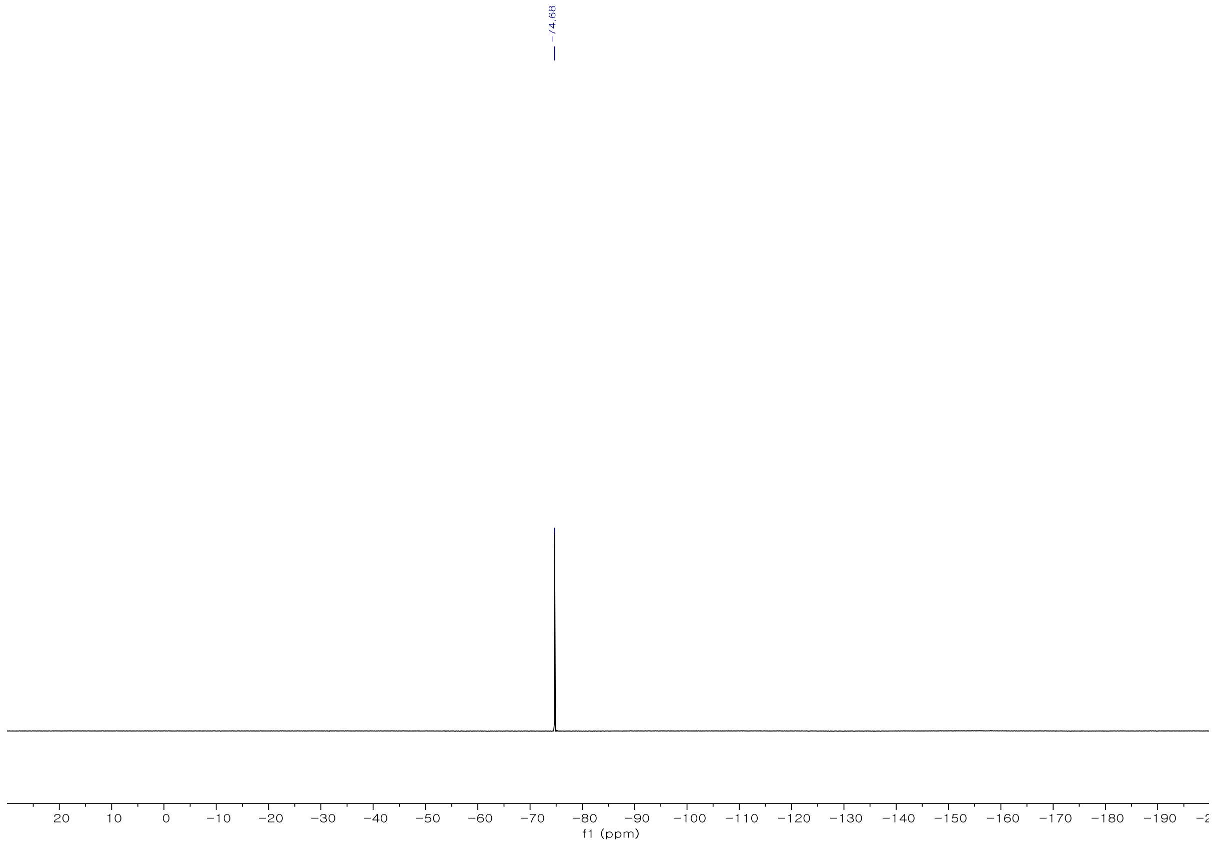




BA-Iridacycle (Scheme 2)






-74.68
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

Appendix II

Crystallographic Data for

BA-Iridacycle and 5a

Crystallographic data of *BA-Iridacycle* (Scheme 2)

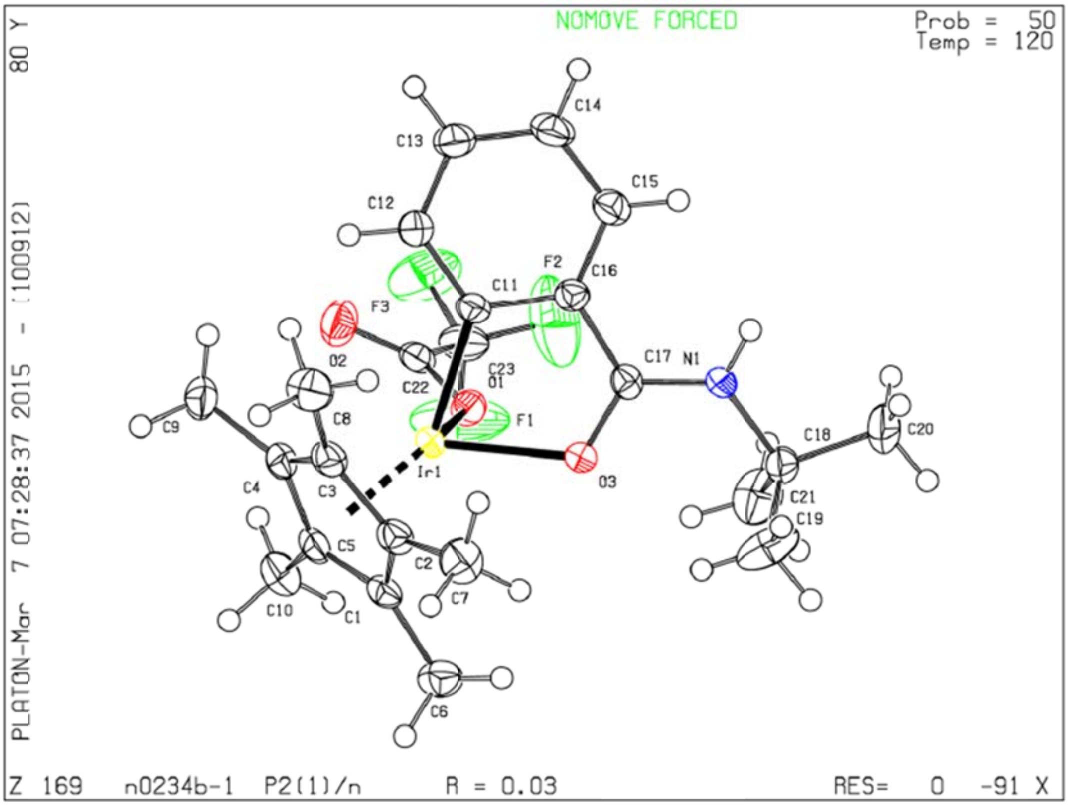


Table S2. Crystal data and structure refinement for ***BA-Iridacycle***.

Identification code	***BA-Iridacycle***	
Empirical formula	C23 H29 F3 Ir N O3	
Formula weight	616.67	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.3407(6) Å	α= 90°.
	b = 15.3465(7) Å	β= 99.774(2)°.
	c = 14.0104(7) Å	γ = 90°.
Volume	2403.0(2) Å^3	
Z	4	
Density (calculated)	1.705 Mg/m^3	
Absorption coefficient	5.602 mm^{-1}	
F(000)	1208	
Crystal size	0.15 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.86 to 36.47°.	
Index ranges	-18<=h<=18, -25<=k<=25, -19<=l<=23	
Reflections collected	90104	
Independent reflections	11697 [R(int) = 0.0680]	
Completeness to theta = 36.47°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6043 and 0.4870	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11697 / 0 / 280	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0663	
R indices (all data)	R1 = 0.0519, wR2 = 0.0791	
Largest diff. peak and hole	1.556 and -1.054 e.Å^{-3}	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for ***BA-Iridacycle***. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	8632(1)	1815(1)	1054(1)	21(1)
F(1)	4372(2)	1555(3)	1220(2)	97(1)
F(2)	4996(2)	2676(2)	2003(3)	98(1)
F(3)	4728(2)	1527(2)	2744(2)	75(1)
O(1)	6858(2)	1987(1)	1316(1)	27(1)
O(2)	6831(2)	939(1)	2438(2)	40(1)
O(3)	8285(2)	3121(1)	582(1)	25(1)
N(1)	8262(2)	4530(1)	1025(1)	26(1)
C(1)	8813(2)	1165(2)	-336(2)	26(1)
C(2)	9940(2)	1506(2)	187(2)	27(1)
C(3)	10221(2)	1065(2)	1104(2)	28(1)
C(4)	9228(2)	492(2)	1187(2)	28(1)
C(5)	8396(2)	547(1)	277(2)	27(1)
C(6)	8204(3)	1452(2)	-1323(2)	36(1)
C(7)	10705(3)	2174(2)	-197(2)	39(1)
C(8)	11347(3)	1154(2)	1829(2)	40(1)
C(9)	9156(3)	-146(2)	1985(2)	37(1)
C(10)	7259(3)	39(2)	67(2)	36(1)
C(11)	9119(2)	2498(2)	2300(2)	24(1)
C(12)	9539(3)	2162(2)	3221(2)	32(1)
C(13)	9832(3)	2703(2)	4016(2)	36(1)
C(14)	9720(3)	3602(2)	3913(2)	35(1)
C(15)	9298(2)	3958(2)	3015(2)	30(1)
C(16)	9000(2)	3407(2)	2221(2)	24(1)
C(17)	8489(2)	3695(1)	1235(2)	22(1)
C(18)	7624(2)	4865(2)	75(2)	29(1)
C(19)	8358(3)	4689(3)	-718(2)	57(1)
C(20)	7434(5)	5833(2)	218(3)	76(2)
C(21)	6411(3)	4427(2)	-185(3)	51(1)
C(22)	6409(2)	1540(2)	1927(2)	25(1)
C(23)	5120(3)	1822(2)	1978(2)	37(1)

Table S4. Bond lengths [Å] and angles [°] for ***BA-Iridacycle***.

Ir(1)-C(11)	2.031(2)
Ir(1)-O(1)	2.1216(18)
Ir(1)-C(2)	2.125(2)
Ir(1)-O(3)	2.1262(15)
Ir(1)-C(3)	2.129(2)
Ir(1)-C(4)	2.138(2)
Ir(1)-C(5)	2.224(2)
Ir(1)-C(1)	2.229(2)
F(1)-C(23)	1.307(4)
F(2)-C(23)	1.318(4)
F(3)-C(23)	1.310(4)
O(1)-C(22)	1.270(3)
O(2)-C(22)	1.215(3)
O(3)-C(17)	1.263(3)
N(1)-C(17)	1.330(3)
N(1)-C(18)	1.494(3)
C(1)-C(5)	1.414(3)
C(1)-C(2)	1.457(4)
C(1)-C(6)	1.502(4)
C(2)-C(3)	1.440(4)
C(2)-C(7)	1.501(4)
C(3)-C(4)	1.448(4)
C(3)-C(8)	1.497(4)
C(4)-C(5)	1.455(4)
C(4)-C(9)	1.499(4)
C(5)-C(10)	1.493(4)
C(11)-C(12)	1.396(4)
C(11)-C(16)	1.404(3)
C(12)-C(13)	1.384(4)
C(13)-C(14)	1.392(4)
C(14)-C(15)	1.381(4)
C(15)-C(16)	1.392(3)
C(16)-C(17)	1.472(3)
C(18)-C(21)	1.519(4)
C(18)-C(20)	1.519(4)
C(18)-C(19)	1.521(4)

C(22)-C(23)	1.538(4)
C(11)-Ir(1)-O(1)	85.10(8)
C(11)-Ir(1)-C(2)	119.52(10)
O(1)-Ir(1)-C(2)	154.30(9)
C(11)-Ir(1)-O(3)	77.85(8)
O(1)-Ir(1)-O(3)	78.78(7)
C(2)-Ir(1)-O(3)	98.20(9)
C(11)-Ir(1)-C(3)	98.38(9)
O(1)-Ir(1)-C(3)	152.10(8)
C(2)-Ir(1)-C(3)	39.56(10)
O(3)-Ir(1)-C(3)	129.08(9)
C(11)-Ir(1)-C(4)	112.29(10)
O(1)-Ir(1)-C(4)	113.49(8)
C(2)-Ir(1)-C(4)	66.22(10)
O(3)-Ir(1)-C(4)	164.02(9)
C(3)-Ir(1)-C(4)	39.69(10)
C(11)-Ir(1)-C(5)	149.91(9)
O(1)-Ir(1)-C(5)	98.92(8)
C(2)-Ir(1)-C(5)	64.03(9)
O(3)-Ir(1)-C(5)	132.23(8)
C(3)-Ir(1)-C(5)	64.77(10)
C(4)-Ir(1)-C(5)	38.91(10)
C(11)-Ir(1)-C(1)	158.48(9)
O(1)-Ir(1)-C(1)	115.96(8)
C(2)-Ir(1)-C(1)	39.02(9)
O(3)-Ir(1)-C(1)	100.93(8)
C(3)-Ir(1)-C(1)	65.39(9)
C(4)-Ir(1)-C(1)	64.96(9)
C(5)-Ir(1)-C(1)	37.03(9)
C(22)-O(1)-Ir(1)	123.34(16)
C(17)-O(3)-Ir(1)	115.54(15)
C(17)-N(1)-C(18)	125.08(19)
C(5)-C(1)-C(2)	106.9(2)
C(5)-C(1)-C(6)	127.3(2)
C(2)-C(1)-C(6)	125.8(2)
C(5)-C(1)-Ir(1)	71.29(13)
C(2)-C(1)-Ir(1)	66.62(13)

C(6)-C(1)-Ir(1)	125.20(17)
C(3)-C(2)-C(1)	108.8(2)
C(3)-C(2)-C(7)	125.9(2)
C(1)-C(2)-C(7)	125.2(2)
C(3)-C(2)-Ir(1)	70.39(13)
C(1)-C(2)-Ir(1)	74.36(13)
C(7)-C(2)-Ir(1)	123.70(18)
C(2)-C(3)-C(4)	107.5(2)
C(2)-C(3)-C(8)	126.7(2)
C(4)-C(3)-C(8)	125.8(2)
C(2)-C(3)-Ir(1)	70.05(13)
C(4)-C(3)-Ir(1)	70.47(13)
C(8)-C(3)-Ir(1)	126.40(18)
C(3)-C(4)-C(5)	106.9(2)
C(3)-C(4)-C(9)	126.8(2)
C(5)-C(4)-C(9)	125.6(2)
C(3)-C(4)-Ir(1)	69.84(13)
C(5)-C(4)-Ir(1)	73.75(13)
C(9)-C(4)-Ir(1)	128.99(17)
C(1)-C(5)-C(4)	109.7(2)
C(1)-C(5)-C(10)	126.7(2)
C(4)-C(5)-C(10)	123.5(2)
C(1)-C(5)-Ir(1)	71.68(13)
C(4)-C(5)-Ir(1)	67.34(12)
C(10)-C(5)-Ir(1)	125.55(17)
C(12)-C(11)-C(16)	117.0(2)
C(12)-C(11)-Ir(1)	127.11(18)
C(16)-C(11)-Ir(1)	115.88(17)
C(13)-C(12)-C(11)	121.3(2)
C(12)-C(13)-C(14)	120.4(2)
C(15)-C(14)-C(13)	119.9(2)
C(14)-C(15)-C(16)	119.2(2)
C(15)-C(16)-C(11)	122.2(2)
C(15)-C(16)-C(17)	124.8(2)
C(11)-C(16)-C(17)	112.9(2)
O(3)-C(17)-N(1)	120.5(2)
O(3)-C(17)-C(16)	117.7(2)
N(1)-C(17)-C(16)	121.8(2)

N(1)-C(18)-C(21)	110.1(2)
N(1)-C(18)-C(20)	106.1(2)
C(21)-C(18)-C(20)	108.8(3)
N(1)-C(18)-C(19)	110.3(2)
C(21)-C(18)-C(19)	109.4(3)
C(20)-C(18)-C(19)	112.2(3)
O(2)-C(22)-O(1)	130.2(2)
O(2)-C(22)-C(23)	118.0(2)
O(1)-C(22)-C(23)	111.9(2)
F(1)-C(23)-F(3)	107.1(3)
F(1)-C(23)-F(2)	106.0(3)
F(3)-C(23)-F(2)	105.6(3)
F(1)-C(23)-C(22)	111.4(2)
F(3)-C(23)-C(22)	113.5(3)
F(2)-C(23)-C(22)	112.8(2)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for ***BA-Iridacycle***. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	27(1)	18(1)	20(1)	-2(1)	5(1)	3(1)
F(1)	38(1)	201(3)	49(1)	-35(2)	2(1)	-16(2)
F(2)	72(2)	56(2)	183(3)	9(2)	71(2)	25(1)
F(3)	62(2)	123(2)	48(1)	15(1)	36(1)	7(2)
O(1)	28(1)	29(1)	25(1)	3(1)	8(1)	6(1)
O(2)	50(1)	31(1)	42(1)	11(1)	16(1)	5(1)
O(3)	35(1)	20(1)	20(1)	-1(1)	4(1)	2(1)
N(1)	43(1)	16(1)	19(1)	-3(1)	2(1)	-3(1)
C(1)	30(1)	24(1)	25(1)	-6(1)	9(1)	3(1)
C(2)	30(1)	26(1)	28(1)	-4(1)	11(1)	1(1)
C(3)	29(1)	27(1)	29(1)	-4(1)	6(1)	8(1)
C(4)	35(1)	21(1)	28(1)	-1(1)	9(1)	7(1)
C(5)	34(1)	18(1)	29(1)	-5(1)	10(1)	4(1)
C(6)	39(2)	43(2)	29(1)	-2(1)	9(1)	2(1)
C(7)	39(2)	37(1)	44(2)	1(1)	15(1)	-5(1)
C(8)	32(1)	49(2)	39(2)	-5(1)	1(1)	10(1)
C(9)	49(2)	26(1)	36(1)	6(1)	12(1)	11(1)
C(10)	37(1)	28(1)	44(2)	-7(1)	9(1)	-3(1)
C(11)	27(1)	25(1)	20(1)	-3(1)	4(1)	4(1)
C(12)	42(2)	28(1)	26(1)	0(1)	3(1)	10(1)
C(13)	41(2)	42(1)	24(1)	-2(1)	1(1)	12(1)
C(14)	37(1)	38(1)	26(1)	-12(1)	-3(1)	4(1)
C(15)	33(1)	27(1)	29(1)	-6(1)	2(1)	-1(1)
C(16)	24(1)	25(1)	23(1)	0(1)	5(1)	1(1)
C(17)	22(1)	20(1)	25(1)	-1(1)	6(1)	-3(1)
C(18)	37(1)	21(1)	28(1)	0(1)	-2(1)	0(1)
C(19)	48(2)	92(3)	31(2)	19(2)	9(1)	3(2)
C(20)	143(4)	22(1)	50(2)	3(1)	-15(2)	9(2)
C(21)	29(1)	58(2)	61(2)	8(2)	-7(1)	3(1)
C(22)	30(1)	23(1)	22(1)	-6(1)	6(1)	-2(1)
C(23)	34(1)	50(2)	29(1)	-5(1)	12(1)	-2(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^{3}) for ***BA-Iridacycle***.

	x	y	z	U(eq)
H(1A)	8506	4915	1482	32
H(6A)	8425	1058	-1814	54
H(6B)	8454	2047	-1446	54
H(6C)	7335	1437	-1351	54
H(7A)	11240	1884	-578	58
H(7B)	11182	2486	345	58
H(7C)	10193	2588	-609	58
H(8A)	11936	727	1685	61
H(8B)	11173	1048	2480	61
H(8C)	11670	1743	1795	61
H(9A)	9506	-702	1834	55
H(9B)	8316	-235	2046	55
H(9C)	9597	82	2596	55
H(10A)	7393	-495	-284	54
H(10B)	6641	392	-329	54
H(10C)	6998	-115	677	54
H(12A)	9626	1549	3303	39
H(13A)	10112	2459	4636	43
H(14A)	9933	3971	4460	42
H(15A)	9212	4571	2939	36
H(19A)	8446	4059	-794	85
H(19B)	9150	4956	-541	85
H(19C)	7950	4939	-1329	85
H(20A)	6942	5916	722	114
H(20B)	7027	6089	-390	114
H(20C)	8210	6119	415	114
H(21A)	5935	4543	323	76
H(21B)	6521	3797	-242	76
H(21C)	5994	4658	-803	76

Table S7. Torsion angles [°] for ***BA-Iridacycle***.

C(11)-Ir(1)-O(1)-C(22)	-78.02(19)
C(2)-Ir(1)-O(1)-C(22)	117.8(2)
O(3)-Ir(1)-O(1)-C(22)	-156.6(2)
C(3)-Ir(1)-O(1)-C(22)	20.6(3)
C(4)-Ir(1)-O(1)-C(22)	34.2(2)
C(5)-Ir(1)-O(1)-C(22)	71.9(2)
C(1)-Ir(1)-O(1)-C(22)	106.61(19)
C(11)-Ir(1)-O(3)-C(17)	-1.57(17)
O(1)-Ir(1)-O(3)-C(17)	85.77(17)
C(2)-Ir(1)-O(3)-C(17)	-120.14(18)
C(3)-Ir(1)-O(3)-C(17)	-92.56(19)
C(4)-Ir(1)-O(3)-C(17)	-132.7(3)
C(5)-Ir(1)-O(3)-C(17)	177.69(16)
C(1)-Ir(1)-O(3)-C(17)	-159.64(17)
C(11)-Ir(1)-C(1)-C(5)	123.7(3)
O(1)-Ir(1)-C(1)-C(5)	-68.97(16)
C(2)-Ir(1)-C(1)-C(5)	118.7(2)
O(3)-Ir(1)-C(1)-C(5)	-151.71(15)
C(3)-Ir(1)-C(1)-C(5)	80.13(16)
C(4)-Ir(1)-C(1)-C(5)	36.21(15)
C(11)-Ir(1)-C(1)-C(2)	5.0(3)
O(1)-Ir(1)-C(1)-C(2)	172.30(13)
O(3)-Ir(1)-C(1)-C(2)	89.56(15)
C(3)-Ir(1)-C(1)-C(2)	-38.59(15)
C(4)-Ir(1)-C(1)-C(2)	-82.52(16)
C(5)-Ir(1)-C(1)-C(2)	-118.7(2)
C(11)-Ir(1)-C(1)-C(6)	-113.3(3)
O(1)-Ir(1)-C(1)-C(6)	54.0(2)
C(2)-Ir(1)-C(1)-C(6)	-118.3(3)
O(3)-Ir(1)-C(1)-C(6)	-28.7(2)
C(3)-Ir(1)-C(1)-C(6)	-156.9(2)
C(4)-Ir(1)-C(1)-C(6)	159.2(3)
C(5)-Ir(1)-C(1)-C(6)	123.0(3)
C(5)-C(1)-C(2)-C(3)	2.1(3)
C(6)-C(1)-C(2)-C(3)	179.9(2)
Ir(1)-C(1)-C(2)-C(3)	62.38(16)

C(5)-C(1)-C(2)-C(7)	179.3(2)
C(6)-C(1)-C(2)-C(7)	-3.0(4)
Ir(1)-C(1)-C(2)-C(7)	-120.5(3)
C(5)-C(1)-C(2)-Ir(1)	-60.23(16)
C(6)-C(1)-C(2)-Ir(1)	117.6(2)
C(11)-Ir(1)-C(2)-C(3)	65.02(17)
O(1)-Ir(1)-C(2)-C(3)	-133.20(19)
O(3)-Ir(1)-C(2)-C(3)	145.65(14)
C(4)-Ir(1)-C(2)-C(3)	-38.10(15)
C(5)-Ir(1)-C(2)-C(3)	-81.10(16)
C(1)-Ir(1)-C(2)-C(3)	-117.1(2)
C(11)-Ir(1)-C(2)-C(1)	-177.90(13)
O(1)-Ir(1)-C(2)-C(1)	-16.1(3)
O(3)-Ir(1)-C(2)-C(1)	-97.27(14)
C(3)-Ir(1)-C(2)-C(1)	117.1(2)
C(4)-Ir(1)-C(2)-C(1)	78.98(15)
C(5)-Ir(1)-C(2)-C(1)	35.98(14)
C(11)-Ir(1)-C(2)-C(7)	-55.7(3)
O(1)-Ir(1)-C(2)-C(7)	106.1(3)
O(3)-Ir(1)-C(2)-C(7)	24.9(2)
C(3)-Ir(1)-C(2)-C(7)	-120.7(3)
C(4)-Ir(1)-C(2)-C(7)	-158.8(3)
C(5)-Ir(1)-C(2)-C(7)	158.2(3)
C(1)-Ir(1)-C(2)-C(7)	122.2(3)
C(1)-C(2)-C(3)-C(4)	-4.1(3)
C(7)-C(2)-C(3)-C(4)	178.9(2)
Ir(1)-C(2)-C(3)-C(4)	60.86(16)
C(1)-C(2)-C(3)-C(8)	174.0(2)
C(7)-C(2)-C(3)-C(8)	-3.1(4)
Ir(1)-C(2)-C(3)-C(8)	-121.1(2)
C(1)-C(2)-C(3)-Ir(1)	-64.93(16)
C(7)-C(2)-C(3)-Ir(1)	118.0(3)
C(11)-Ir(1)-C(3)-C(2)	-127.13(15)
O(1)-Ir(1)-C(3)-C(2)	137.50(18)
O(3)-Ir(1)-C(3)-C(2)	-46.01(18)
C(4)-Ir(1)-C(3)-C(2)	117.9(2)
C(5)-Ir(1)-C(3)-C(2)	79.05(15)
C(1)-Ir(1)-C(3)-C(2)	38.07(14)

C(11)-Ir(1)-C(3)-C(4)	115.01(15)
O(1)-Ir(1)-C(3)-C(4)	19.6(3)
C(2)-Ir(1)-C(3)-C(4)	-117.9(2)
O(3)-Ir(1)-C(3)-C(4)	-163.87(13)
C(5)-Ir(1)-C(3)-C(4)	-38.80(14)
C(1)-Ir(1)-C(3)-C(4)	-79.79(15)
C(11)-Ir(1)-C(3)-C(8)	-5.7(3)
O(1)-Ir(1)-C(3)-C(8)	-101.1(3)
C(2)-Ir(1)-C(3)-C(8)	121.4(3)
O(3)-Ir(1)-C(3)-C(8)	75.4(3)
C(4)-Ir(1)-C(3)-C(8)	-120.7(3)
C(5)-Ir(1)-C(3)-C(8)	-159.5(3)
C(1)-Ir(1)-C(3)-C(8)	159.5(3)
C(2)-C(3)-C(4)-C(5)	4.4(2)
C(8)-C(3)-C(4)-C(5)	-173.7(2)
Ir(1)-C(3)-C(4)-C(5)	64.95(15)
C(2)-C(3)-C(4)-C(9)	175.2(2)
C(8)-C(3)-C(4)-C(9)	-2.9(4)
Ir(1)-C(3)-C(4)-C(9)	-124.2(2)
C(2)-C(3)-C(4)-Ir(1)	-60.59(16)
C(8)-C(3)-C(4)-Ir(1)	121.4(2)
C(11)-Ir(1)-C(4)-C(3)	-75.68(16)
O(1)-Ir(1)-C(4)-C(3)	-170.12(13)
C(2)-Ir(1)-C(4)-C(3)	37.98(14)
O(3)-Ir(1)-C(4)-C(3)	51.6(4)
C(5)-Ir(1)-C(4)-C(3)	115.5(2)
C(1)-Ir(1)-C(4)-C(3)	80.99(15)
C(11)-Ir(1)-C(4)-C(5)	168.83(14)
O(1)-Ir(1)-C(4)-C(5)	74.38(15)
C(2)-Ir(1)-C(4)-C(5)	-77.52(15)
O(3)-Ir(1)-C(4)-C(5)	-63.9(4)
C(3)-Ir(1)-C(4)-C(5)	-115.5(2)
C(1)-Ir(1)-C(4)-C(5)	-34.50(14)
C(11)-Ir(1)-C(4)-C(9)	45.9(3)
O(1)-Ir(1)-C(4)-C(9)	-48.5(3)
C(2)-Ir(1)-C(4)-C(9)	159.6(3)
O(3)-Ir(1)-C(4)-C(9)	173.1(3)
C(3)-Ir(1)-C(4)-C(9)	121.6(3)

C(5)-Ir(1)-C(4)-C(9)	-122.9(3)
C(1)-Ir(1)-C(4)-C(9)	-157.4(3)
C(2)-C(1)-C(5)-C(4)	0.6(3)
C(6)-C(1)-C(5)-C(4)	-177.1(2)
Ir(1)-C(1)-C(5)-C(4)	-56.65(15)
C(2)-C(1)-C(5)-C(10)	178.4(2)
C(6)-C(1)-C(5)-C(10)	0.7(4)
Ir(1)-C(1)-C(5)-C(10)	121.1(2)
C(2)-C(1)-C(5)-Ir(1)	57.27(15)
C(6)-C(1)-C(5)-Ir(1)	-120.5(2)
C(3)-C(4)-C(5)-C(1)	-3.1(2)
C(9)-C(4)-C(5)-C(1)	-174.1(2)
Ir(1)-C(4)-C(5)-C(1)	59.24(16)
C(3)-C(4)-C(5)-C(10)	179.0(2)
C(9)-C(4)-C(5)-C(10)	8.0(4)
Ir(1)-C(4)-C(5)-C(10)	-118.6(2)
C(3)-C(4)-C(5)-Ir(1)	-62.35(15)
C(9)-C(4)-C(5)-Ir(1)	126.7(2)
C(11)-Ir(1)-C(5)-C(1)	-142.51(18)
O(1)-Ir(1)-C(5)-C(1)	121.84(14)
C(2)-Ir(1)-C(5)-C(1)	-37.89(15)
O(3)-Ir(1)-C(5)-C(1)	38.93(19)
C(3)-Ir(1)-C(5)-C(1)	-81.97(16)
C(4)-Ir(1)-C(5)-C(1)	-121.6(2)
C(11)-Ir(1)-C(5)-C(4)	-21.0(3)
O(1)-Ir(1)-C(5)-C(4)	-116.61(14)
C(2)-Ir(1)-C(5)-C(4)	83.66(16)
O(3)-Ir(1)-C(5)-C(4)	160.48(14)
C(3)-Ir(1)-C(5)-C(4)	39.58(15)
C(1)-Ir(1)-C(5)-C(4)	121.6(2)
C(11)-Ir(1)-C(5)-C(10)	95.0(3)
O(1)-Ir(1)-C(5)-C(10)	-0.7(2)
C(2)-Ir(1)-C(5)-C(10)	-160.4(3)
O(3)-Ir(1)-C(5)-C(10)	-83.6(2)
C(3)-Ir(1)-C(5)-C(10)	155.5(3)
C(4)-Ir(1)-C(5)-C(10)	115.9(3)
C(1)-Ir(1)-C(5)-C(10)	-122.5(3)
O(1)-Ir(1)-C(11)-C(12)	98.9(2)

C(2)-Ir(1)-C(11)-C(12)	-88.9(3)
O(3)-Ir(1)-C(11)-C(12)	178.5(3)
C(3)-Ir(1)-C(11)-C(12)	-53.2(2)
C(4)-Ir(1)-C(11)-C(12)	-14.5(3)
C(5)-Ir(1)-C(11)-C(12)	-0.4(4)
C(1)-Ir(1)-C(11)-C(12)	-92.5(3)
O(1)-Ir(1)-C(11)-C(16)	-80.11(18)
C(2)-Ir(1)-C(11)-C(16)	92.07(19)
O(3)-Ir(1)-C(11)-C(16)	-0.55(17)
C(3)-Ir(1)-C(11)-C(16)	127.78(18)
C(4)-Ir(1)-C(11)-C(16)	166.49(17)
C(5)-Ir(1)-C(11)-C(16)	-179.46(17)
C(1)-Ir(1)-C(11)-C(16)	88.5(3)
C(16)-C(11)-C(12)-C(13)	-0.4(4)
Ir(1)-C(11)-C(12)-C(13)	-179.4(2)
C(11)-C(12)-C(13)-C(14)	-0.4(4)
C(12)-C(13)-C(14)-C(15)	0.9(4)
C(13)-C(14)-C(15)-C(16)	-0.5(4)
C(14)-C(15)-C(16)-C(11)	-0.3(4)
C(14)-C(15)-C(16)-C(17)	177.0(2)
C(12)-C(11)-C(16)-C(15)	0.8(4)
Ir(1)-C(11)-C(16)-C(15)	179.9(2)
C(12)-C(11)-C(16)-C(17)	-176.9(2)
Ir(1)-C(11)-C(16)-C(17)	2.3(3)
Ir(1)-O(3)-C(17)-N(1)	-177.55(18)
Ir(1)-O(3)-C(17)-C(16)	3.3(3)
C(18)-N(1)-C(17)-O(3)	8.0(4)
C(18)-N(1)-C(17)-C(16)	-172.9(2)
C(15)-C(16)-C(17)-O(3)	178.7(2)
C(11)-C(16)-C(17)-O(3)	-3.7(3)
C(15)-C(16)-C(17)-N(1)	-0.4(4)
C(11)-C(16)-C(17)-N(1)	177.1(2)
C(17)-N(1)-C(18)-C(21)	55.4(4)
C(17)-N(1)-C(18)-C(20)	172.9(3)
C(17)-N(1)-C(18)-C(19)	-65.4(3)
Ir(1)-O(1)-C(22)-O(2)	-2.9(4)
Ir(1)-O(1)-C(22)-C(23)	178.71(16)
O(2)-C(22)-C(23)-F(1)	-104.5(3)

O(1)-C(22)-C(23)-F(1)	74.2(3)
O(2)-C(22)-C(23)-F(3)	16.5(4)
O(1)-C(22)-C(23)-F(3)	-164.9(3)
O(2)-C(22)-C(23)-F(2)	136.4(3)
O(1)-C(22)-C(23)-F(2)	-44.9(4)

Symmetry transformations used to generate equivalent atoms:

Crystallographic data of 5a (Table 4)

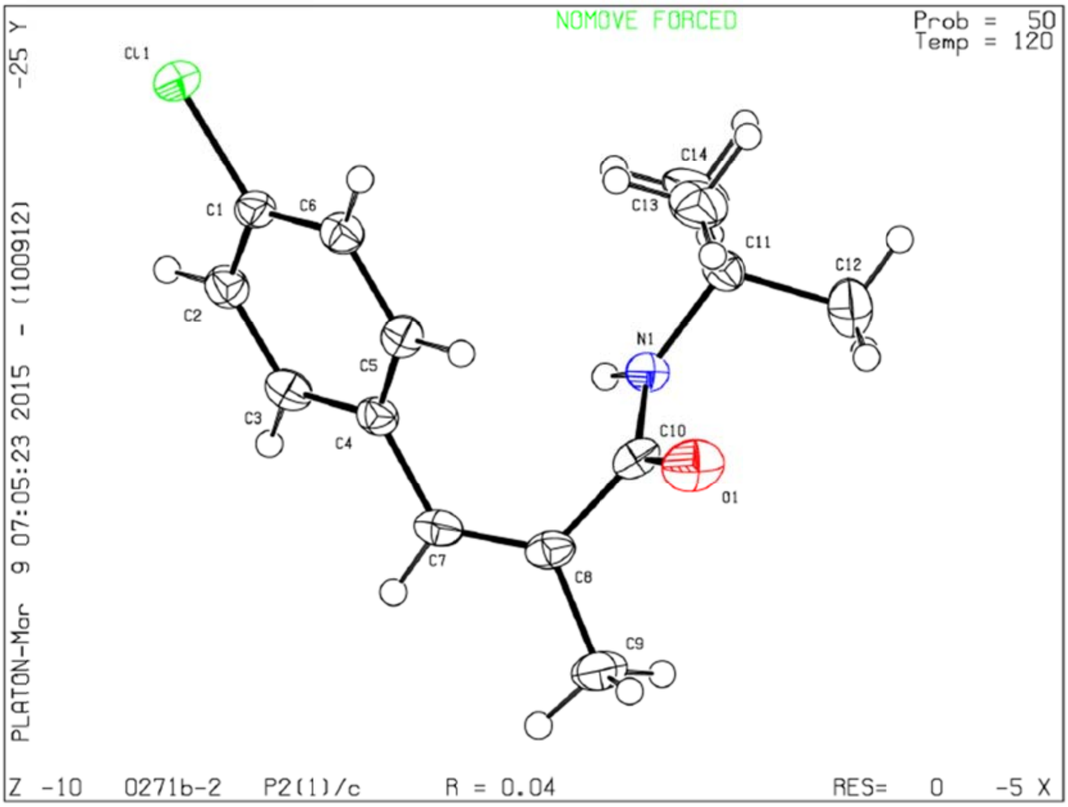


Table S8. Crystal data and structure refinement for **5a**.

Identification code	**5a**	
Empirical formula	C14 H18 Cl N O	
Formula weight	251.74	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.401(3) Å	α= 90°.
	b = 8.6470(17) Å	β= 100.955(3)°.
	c = 9.4509(18) Å	γ = 90°.
Volume	1396.2(5) $Å^3$	
Z	4	
Density (calculated)	1.198 Mg/m^3	
Absorption coefficient	0.259 mm^{-1}	
F(000)	536	
Crystal size	0.15 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.38 to 26.43°.	
Index ranges	-21<=h<=21, -10<=k<=10, -11<=l<=11	
Reflections collected	21802	
Independent reflections	2847 [R(int) = 0.0538]	
Completeness to theta = 26.43°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9796 and 0.9623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2847 / 0 / 154	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0826	
R indices (all data)	R1 = 0.0477, wR2 = 0.0891	
Largest diff. peak and hole	0.232 and -0.203 e.$Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	429(1)	13321(1)	4575(1)	30(1)
O(1)	3214(1)	7408(1)	8519(1)	38(1)
N(1)	3294(1)	8557(1)	6393(1)	22(1)
C(1)	827(1)	11468(2)	4857(2)	23(1)
C(2)	713(1)	10417(2)	3736(2)	26(1)
C(3)	1019(1)	8939(2)	3985(2)	26(1)
C(4)	1442(1)	8505(2)	5328(2)	23(1)
C(5)	1536(1)	9591(2)	6442(2)	24(1)
C(6)	1235(1)	11072(2)	6213(2)	24(1)
C(7)	1745(1)	6907(2)	5551(2)	26(1)
C(8)	2410(1)	6434(2)	6378(2)	26(1)
C(9)	2612(1)	4744(2)	6610(2)	38(1)
C(10)	3007(1)	7518(2)	7195(2)	24(1)
C(11)	3873(1)	9775(2)	6925(2)	26(1)
C(12)	4656(1)	9044(2)	7567(2)	50(1)
C(13)	3584(1)	10791(2)	8035(2)	40(1)
C(14)	3940(1)	10749(2)	5613(2)	47(1)

Table S10. Bond lengths [Å] and angles [°] for **5a**.

Cl(1)-C(1)	1.7456(16)
O(1)-C(10)	1.2381(19)
N(1)-C(10)	1.3318(19)
N(1)-C(11)	1.479(2)
C(1)-C(2)	1.381(2)
C(1)-C(6)	1.385(2)
C(2)-C(3)	1.387(2)
C(3)-C(4)	1.393(2)
C(4)-C(5)	1.397(2)
C(4)-C(7)	1.479(2)
C(5)-C(6)	1.385(2)
C(7)-C(8)	1.331(2)
C(8)-C(10)	1.500(2)
C(8)-C(9)	1.509(2)
C(11)-C(12)	1.519(2)
C(11)-C(14)	1.523(2)
C(11)-C(13)	1.525(2)
C(10)-N(1)-C(11)	126.30(13)
C(2)-C(1)-C(6)	121.37(14)
C(2)-C(1)-Cl(1)	119.47(12)
C(6)-C(1)-Cl(1)	119.15(12)
C(1)-C(2)-C(3)	118.79(15)
C(2)-C(3)-C(4)	121.51(15)
C(3)-C(4)-C(5)	118.11(14)
C(3)-C(4)-C(7)	119.60(14)
C(5)-C(4)-C(7)	122.23(14)
C(6)-C(5)-C(4)	121.19(15)
C(5)-C(6)-C(1)	119.03(14)
C(8)-C(7)-C(4)	128.09(15)
C(7)-C(8)-C(10)	123.34(14)
C(7)-C(8)-C(9)	122.42(15)
C(10)-C(8)-C(9)	114.21(14)
O(1)-C(10)-N(1)	123.94(15)
O(1)-C(10)-C(8)	120.82(14)
N(1)-C(10)-C(8)	115.24(13)

N(1)-C(11)-C(12)	109.94(14)
N(1)-C(11)-C(14)	105.68(12)
C(12)-C(11)-C(14)	110.69(16)
N(1)-C(11)-C(13)	110.58(13)
C(12)-C(11)-C(13)	110.67(15)
C(14)-C(11)-C(13)	109.17(15)

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2$x 10^3) for **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	32(1)	22(1)	37(1)	3(1)	5(1)	3(1)
O(1)	58(1)	38(1)	20(1)	7(1)	8(1)	-1(1)
N(1)	27(1)	21(1)	16(1)	0(1)	3(1)	-1(1)
C(1)	22(1)	20(1)	30(1)	3(1)	7(1)	-1(1)
C(2)	27(1)	27(1)	24(1)	2(1)	3(1)	-4(1)
C(3)	29(1)	25(1)	25(1)	-4(1)	6(1)	-6(1)
C(4)	22(1)	21(1)	28(1)	0(1)	8(1)	-3(1)
C(5)	24(1)	26(1)	24(1)	2(1)	6(1)	1(1)
C(6)	25(1)	24(1)	25(1)	-3(1)	7(1)	-1(1)
C(7)	31(1)	19(1)	31(1)	-2(1)	12(1)	-5(1)
C(8)	32(1)	20(1)	28(1)	4(1)	13(1)	0(1)
C(9)	44(1)	21(1)	50(1)	3(1)	11(1)	1(1)
C(10)	31(1)	21(1)	23(1)	3(1)	10(1)	7(1)
C(11)	26(1)	25(1)	25(1)	-3(1)	1(1)	-3(1)
C(12)	29(1)	48(1)	68(1)	-6(1)	-4(1)	3(1)
C(13)	46(1)	32(1)	42(1)	-15(1)	9(1)	-4(1)
C(14)	61(1)	41(1)	37(1)	1(1)	5(1)	-27(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **5a**.

	x	y	z	U(eq)
H(1A)	3122	8514	5456	26
H(2A)	430	10700	2812	31
H(3A)	938	8206	3222	31
H(5A)	1811	9309	7373	29
H(6A)	1308	11806	6975	29
H(7A)	1425	6121	5041	32
H(9A)	2199	4112	6040	57
H(9B)	2660	4491	7633	57
H(9C)	3110	4533	6307	57
H(12A)	4600	8422	8409	75
H(12B)	5045	9858	7861	75
H(12C)	4827	8380	6845	75
H(13A)	3082	11259	7600	60
H(13B)	3968	11608	8356	60
H(13C)	3516	10159	8864	60
H(14A)	3431	11210	5215	70
H(14B)	4108	10093	4882	70
H(14C)	4326	11572	5897	70

Table S13. Torsion angles [°] for **5a**.

C(6)-C(1)-C(2)-C(3)	-0.2(2)
Cl(1)-C(1)-C(2)-C(3)	-178.73(11)
C(1)-C(2)-C(3)-C(4)	-0.7(2)
C(2)-C(3)-C(4)-C(5)	1.6(2)
C(2)-C(3)-C(4)-C(7)	178.85(14)
C(3)-C(4)-C(5)-C(6)	-1.6(2)
C(7)-C(4)-C(5)-C(6)	-178.82(14)
C(4)-C(5)-C(6)-C(1)	0.8(2)
C(2)-C(1)-C(6)-C(5)	0.2(2)
Cl(1)-C(1)-C(6)-C(5)	178.68(11)
C(3)-C(4)-C(7)-C(8)	145.40(17)
C(5)-C(4)-C(7)-C(8)	-37.5(2)
C(4)-C(7)-C(8)-C(10)	-3.5(3)
C(4)-C(7)-C(8)-C(9)	174.38(15)
C(11)-N(1)-C(10)-O(1)	-2.4(2)
C(11)-N(1)-C(10)-C(8)	178.59(13)
C(7)-C(8)-C(10)-O(1)	122.78(18)
C(9)-C(8)-C(10)-O(1)	-55.3(2)
C(7)-C(8)-C(10)-N(1)	-58.2(2)
C(9)-C(8)-C(10)-N(1)	123.72(15)
C(10)-N(1)-C(11)-C(12)	66.2(2)
C(10)-N(1)-C(11)-C(14)	-174.26(15)
C(10)-N(1)-C(11)-C(13)	-56.2(2)

Symmetry transformations used to generate equivalent atoms: