Supporting Information

N-Iminopyridinium Ylide-Directed, Cobalt-Catalyzed Coupling of sp^2 C-H Bonds with Alkynes

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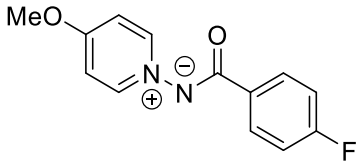
General Information.

The ^{1}H, ^{13}C NMR spectra were recorded on JEOL EC-400, EC-500 and EC-600 spectrometers using either residual tetramethylsilane or residual solvent peaks as a reference. Compounds for HRMS were analyzed by positive mode electrospray ionization (CI or ESI) using Agilent QTOF mass spectrometer in the Mass Spectrometry Facility (MSF) of the Department of Chemistry and Biochemistry of University of Texas-Austin. Column chromatography was performed using a Biotage Isolera instrument with 60Å silica gel. Reagents and starting materials were purchased from commercial vendors and used without further purification. Complexes $[Cp^*Co(CO)I_2]$,[1a] $[Cp^*Co(MeCN)_3][SbF_6]_2$[1b] and $[CpCo(MeCN)_3[SbF_6]_2$[1b] were prepared according to the reported procedure.

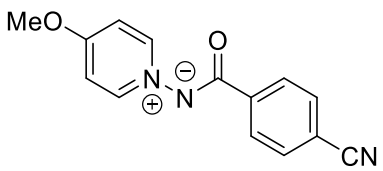
Preparation and Characterization of Pyridinium Ylides.

Pyridinium ylides were prepared according to the literature procedures.[2] Procedures and characterization data for unknown pyridinium ylides are described below.



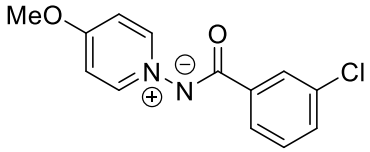
(4-Fluorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (Method A)

To a 100 mL round bottomed flask were added 4-methoxypyridine (0.41 mL, 4 mmol) and CH_2Cl_2 (20 mL). *O*-(2,4,6-Trimethylbenzenesulfonyl)hydroxylamine (1.03 g, 4.8 mmol)[2b] was added to the solution, and the mixture was stirred for 2 h. This step prepares a substituted 1-aminopyridine. To another 100 mL round bottomed flask were added 4-fluorobenzoic acid (0.56 g, 4 mmol) and CH_2Cl_2 (20 mL), and the mixture was cooled to 0 °C. Ethyl chloroformate (0.42 mL, 4.4 mmol) was added to the mixture followed by the addition of triethylamine (1.67 mL, 12 mmol). The mixture was stirred for 30 min at room temperature. To this mixture were added the 1-aminopyridinium solution prepared above dropwise and solid K_2CO_3 (1.66 g, 12 mmol). After stirring the mixture for 24 h, NaOH (50 mL of a 1 N aqueous solution) was poured in and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The extracts were dried over $MgSO_4$, and the residue was purified by column chromatography (gradient elution, EtOAc/MeOH, 0% → 15%) to give the product (0.44 g, 45%). Appearance: white solid; mp 212− 213 °C (EtOAc/MeOH = 10:1); R_f = 0.33 (EtOAc/MeOH = 5/1); ^{1}H NMR (400 MHz, MeOD) δ 8.46 (d, J = 7.0 Hz, 2H), 8.10 – 8.00 (m, 2H), 7.43 (d, J = 7.0 Hz, 2H), 7.19 – 7.03 (m, 2H), 4.10 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 173.1, 169.4, 165.8 (d, J = 248.2 Hz), 146.4, 134.1 (d, J = 3.1 Hz), 131.3 (d, J = 8.7 Hz), 115.7 (d, J = 21.8 Hz), 113.6, 58.0. HRMS (ESI) calcd for $C_{13}H_{11}FN_2O_2$ $[M + Na]^+$ 269.0697, found 269.0697.



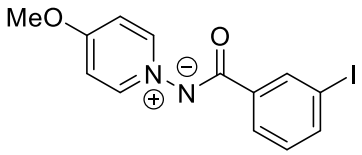
(4-Cyanobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

Method A was employed, with 4-cyanobenzoic acid (0.59 g, 4 mmol). Yield: 0.42 g, 41%; Appearance: light yellow solid; mp 221− 222 °C (EtOAc/MeOH = 10:1); R_f = 0.31 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.8 Hz, 2H), 8.23 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 6.8 Hz, 2H), 4.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 166.4, 144.8, 142.1, 131.8, 128.6, 119.2, 113.3, 111.7, 57.1. HRMS (ESI) calcd for $C_{14}H_{11}N_3O_2$ [M + Na]$^+$ 276.0743, found 276.0750.



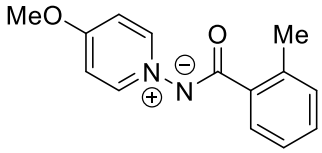
(3-Chlorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

Method A was employed, with 3-chlorobenzoic acid (0.63 g, 4 mmol). Yield: 0.78 g, 74%; Appearance: white solid; mp 154−155 °C (EtOAc/MeOH = 10:1); R_f = 0.38 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, MeOD) δ 8.47 (d, J = 6.2 Hz, 2H), 8.01 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.51 – 7.35 (m, 4H), 4.10 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 172.5, 169.4, 146.3, 140.1, 135.0, 131.4, 130.6, 129.0, 127.3, 113.6, 58.0. HRMS (ESI) calcd for $C_{13}H_{11}N_2O_2Cl$ [M + Na]$^+$ 285.0401, found 285.0403.



(3-Iodobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

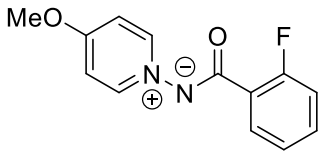
Method A was employed, with 3-iodobenzoic acid (0.99 g, 4 mmol). Yield: 0.89 g, 63%; Appearance: white solid; mp 135−136 °C (EtOAc/MeOH = 10:1); R_f = 0.40 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.46 (m, 3H), 8.09 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 7.4 Hz, 2H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 166.2, 145.0, 139.7, 138.9, 137.0, 129.8, 127.3, 111.6, 93.9, 57.0. HRMS (ESI) calcd for $C_{13}H_{11}N_2O_2I$ [M + Na]$^+$ 376.9757, found 376.9753.



(4-Methoxypyridin-1-ium-1-yl)(2-methylbenzoyl)amide

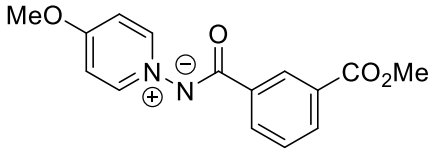
Method A was employed, with 2-methylbenzoic acid (0.54 g, 4 mmol). Yield: 0.53 g, 55%; Appearance: white solid; mp 163−164 °C (EtOAc/MeOH = 10:1); R_f = 0.22 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 7.4 Hz, 2H), 7.67 (d, J = 7.0 Hz, 1H), 7.26

– 7.14 (m, 3H), 7.04 (d, *J* = 7.4 Hz, 2H), 3.96 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 166.0, 144.9, 138.7, 136.4, 130.6, 128.4, 128.2, 125.4, 111.5, 56.9, 20.5. HRMS (ESI) calcd for $C_{14}H_{14}N_2O_2$ $[M + Na]^+$ 265.0947, found 265.0943.



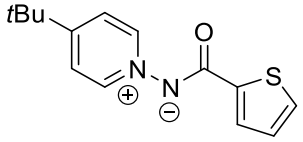
(2-Fluorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

Method A was employed, with 2-fluorobenzoic acid (0.56 g, 4 mmol). Yield: 0.67 g, 68%; Appearance: white solid; mp 141−142 °C (EtOAc/MeOH = 10:1); R_f = 0.24 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.6 Hz, 2H), 7.89 (td, *J* = 7.5, 1.7 Hz, 1H), 7.39 – 7.30 (m, 1H), 7.16 (td, *J* = 7.5, 0.9 Hz, 1H), 7.13 – 7.03 (m, 3H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 166.3, 160.7 (d, *J* = 251.2 Hz), 145.0, 130.9 (d, *J* = 3.2 Hz), 130.7 (d, *J* = 8.4 Hz), 126.4 (d, *J* = 13.2 Hz), 123.7 (d, *J* = 3.7 Hz), 116.3 (d, *J* = 23.2 Hz), 111.5, 57.0. HRMS (ESI) calcd for $C_{13}H_{11}N_2O_2F$ $[M + Na]^+$ 269.0697, found 269.0700.



(3-(Methoxycarbonyl)benzoyl)(4-methoxypyridin-1-ium-1-yl)amide

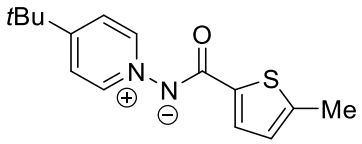
Method A was employed, with 3-(methoxycarbonyl)benzoic acid (0.72 g, 4 mmol). Yield: 0.84 g, 73%; Appearance: white solid; mp 170−171 °C (EtOAc/MeOH = 10:1); R_f = 0.29 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, MeOD) δ 8.69 (s, 1H), 8.49 (d, *J* = 6.4 Hz, 2H), 8.25 (d, *J* = 7.7 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 6.5 Hz, 2H), 4.10 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 172.9, 169.4, 168.2, 146.4, 138.5, 133.5, 132.3, 131.2, 130.1, 129.4, 113.6, 58.0, 52.7. HRMS (ESI) calcd for $C_{15}H_{14}N_2O_4$ $[M + Na]^+$ 309.0846, found 309.0848.



(4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-2-carbonyl)amide

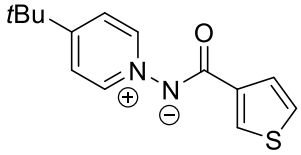
Method A was employed, with 2-thiophenecarboxylic acid (0.51 g, 4 mmol). Yield: 0.53 g, 51%; Appearance: white solid; mp 225− 226 °C (EtOAc/MeOH = 10:1); R_f = 0.52 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.2 Hz, 2H), 7.76 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.60 (d, *J* = 7.1 Hz, 2H), 7.36 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.6 Hz, 1H), 1.39 (s, 9H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 166.9, 163.0, 142.6, 141.8, 129.0, 128.1, 127.2, 123.1, 35.8, 30.3. HRMS (ESI) calcd for $C_{14}H_{16}N_2OS$ $[M + H]^+$ 261.1056, found 261.1053.



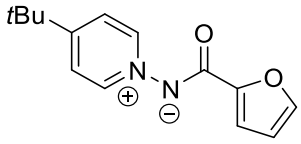
(4-(tert-Butyl)pyridin-1-ium-1-yl)(5-methylthiophene-2-carbonyl)amide

Method A was employed, with 5-methylthiophene-2-carboxylic acid (0.57 g, 4 mmol). Yield: 0.75 g, 68%; appearance: white solid; mp 194−195 °C (EtOAc/MeOH = 10:1); R_f = 0.52 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 7.1 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 7.55 (d, J = 3.5 Hz, 1H), 6.73 (d, J = 3.5 Hz, 1H), 2.50 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 162.7, 142.9, 142.6, 139.2, 129.2, 125.6, 123.0, 35.8, 30.3, 15.8. HRMS (ESI) calcd for $C_{15}H_{18}N_2OS$ $[M + H]^+$ 275.1213, found 275.1209.



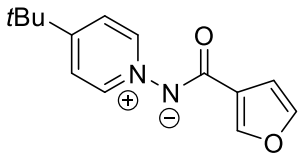
(4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-3-carbonyl)amide

Method A was employed, with thiophene-3-carboxylic acid (0.51 g, 4 mmol). Yield: 0.79 g, 76%; appearance: white solid; mp 244−245 °C (EtOAc/MeOH = 10:1); R_f = 0.38 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 7.2 Hz, 2H), 8.01 (dd, J = 3.1, 1.2 Hz, 1H), 7.63 (dd, J = 4.9, 1.2 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.28 (dd, J = 4.9, 3.1 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 162.8, 142.7, 141.0, 127.7, 127.4, 124.9, 123.1, 35.8, 30.3. HRMS (ESI) calcd for $C_{14}H_{16}N_2OS$ $[M + H]^+$ 261.1056, found 261.1054.



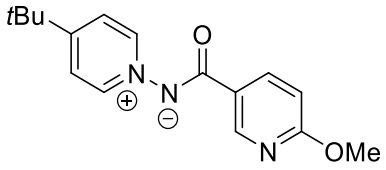
(4-(tert-Butyl)pyridin-1-ium-1-yl)(furan-2-carbonyl)amide

Method A was employed, with furan-2-carboxylic acid (0.45 g, 4 mmol), Yield: 0.79 g, 81%; appearance: white solid; mp 220−221 °C (EtOAc/MeOH = 10:1); R_f = 0.29 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 7.2 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 0.8 Hz, 1H), 7.07 (dd, J = 3.4, 0.8 Hz, 1H), 6.47 (dd, J = 3.4, 1.8 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 163.0, 151.4, 143.4, 142.6, 123.2, 112.7, 111.2, 35.8, 30.3. HRMS (ESI) calcd for $C_{14}H_{16}N_2O_2$ $[M + H]^+$ 245.1285, found 245.1280.



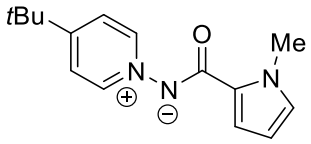
(4-(tert-Butyl)pyridin-1-ium-1-yl)(furan-3-carbonyl)amide

Method A was employed, with furan-3-carboxylic acid (0.45 g, 4 mmol), Yield: 0.57 g, 58%; appearance: white solid; mp 242−243 °C (EtOAc/MeOH = 10:1); R_f = 0.36 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 7.1 Hz, 2H), 8.00 (d, J = 1.6 Hz, 1H), 7.61 (d, J = 7.1 Hz, 2H), 7.42 (s, 1H), 6.82 (d, J = 1.6 Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 162.9, 144.5, 142.8, 142.7, 125.3, 123.1, 109.9, 35.7, 30.3. HRMS (ESI) calcd for $C_{14}H_{16}N_2O_2$ $[M + H]^+$ 245.1285, found 245.1281.



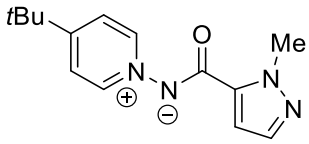
(4-(tert-Butyl)pyridin-1-ium-1-yl)(6-methoxynicotinoyl)amide

Method A was employed, with 6-methoxynicotinic acid (4 mmol, 0.61 g), Yield: 0.78 g, 68%; appearance: white solid; mp 180−181 °C (EtOAc/MeOH = 10:1); R_f = 0.33 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 2.3 Hz, 1H), 8.64 (d, J = 7.1 Hz, 2H), 8.30 (dd, J = 8.6, 2.3 Hz, 1H), 7.62 (d, J = 7.1 Hz, 2H), 6.75 (d, J = 8.6 Hz, 1H), 3.99 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 165.3, 162.9, 147.8, 142.7, 138.6, 126.4, 123.1, 109.7, 53.7, 35.8, 30.3. HRMS (ESI) calcd for $C_{16}H_{19}N_3O_2$ $[M + H]^+$ 286.1550, found 286.1548.



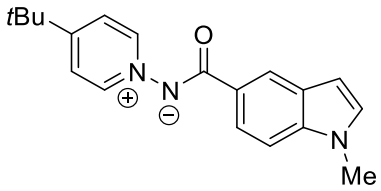
(4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-pyrrole-2-carbonyl)amide

Method A was employed, with 1-methyl-1H-pyrrole-2-carboxylic acid (4 mmol, 0.50 g), Yield: 0.45 g, 44%; appearance: white solid; mp 214−215 °C (EtOAc/MeOH = 10:1); R_f = 0.36 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 7.1 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 6.84 (dd, J = 3.8, 1.9 Hz, 1H), 6.73 – 6.63 (m, 1H), 6.11 (dd, J = 3.8, 2.5 Hz, 1H), 3.99 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 162.4, 142.9, 128.8, 126.3, 123.0, 112.3, 106.9, 36.9, 35.6, 30.3. HRMS (ESI) calcd for $C_{15}H_{19}N_3O$ $[M + H]^+$ 258.1601, found 258.1594.



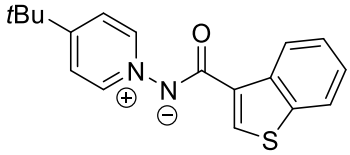
(4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-pyrazole-5-carbonyl)amide

Method A was employed, with 1-methyl-1H-pyrazole-5-carboxylic acid (4 mmol, 0.50 g), Yield: 0.66 g, 64%; appearance: white solid; mp 177−178 °C (EtOAc/MeOH = 10:1); R_f = 0.24 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 6.9 Hz, 2H), 7.64 (d, J = 6.9 Hz, 2H), 7.44 (d, J = 2.0 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 4.24 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 163.6, 142.6, 138.8, 137.5, 123.3, 107.5, 39.4, 35.9, 30.3. HRMS (ESI) calcd for $C_{14}H_{18}N_4O$ $[M + H]^+$ 259.1553, found 259.1551



(4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-indole-5-carbonyl)amide

Method A was employed, with 1-methyl-1H-indole-5-carboxylic acid (4 mmol, 0.70 g). Yield: 0.98 g, 80%; appearance: pale yellow solid; mp 218−219 °C (EtOAc/MeOH = 10:1); R_f = 0.38 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 6.7 Hz, 2H), 8.51 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 6.7 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 3.3 Hz, 1H), 6.55 (*d*, J = 3.2 Hz, 1H), 3.79 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 162.3, 143.0, 138.1, 129.3, 128.6, 128.1, 123.0, 122.1, 121.5, 108.4, 102.1, 35.6, 33.0, 30.3. HRMS (ESI) calcd for $C_{19}H_{21}N_3O$ $[M + H]^+$ 308.1757, found 308.1758

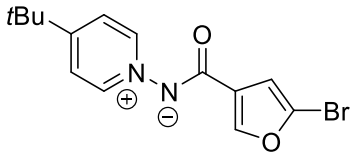


(Benzo[b]thiophene-3-carbonyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide

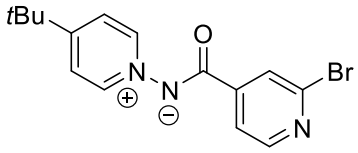
Method A was employed, with benzo[b]thiophene-3-carboxylic acid (4 mmol, 0.71 g) Yield: 0.92 g, 74%; appearance: white solid; mp 179−180 °C (EtOAc/MeOH = 10:1); R_f = 0.52 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 8.0 Hz, 1H), 8.68 (d, J = 6.5 Hz, 2H), 8.26 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 6.5 Hz, 2H), 7.47 – 7.37 (m, 1H), 7.38 – 7.30 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 162.9, 142.8, 140.7, 137.7, 134.6, 130.4, 125.9, 124.4, 124.1, 123.1, 122.4, 35.7, 30.3. HRMS (ESI) calcd for $C_{18}H_{18}N_2OS$ $[M + H]^+$ 311.1213, found 311.1214

Preparation of pyridinium ylides (Method B)

(5-Bromofuran-3-carbonyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide

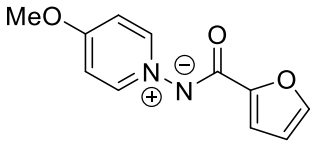


To a 100 mL round bottomed flask were added 4-tert-butylpyridine (0.59 mL, 4 mmol) and CH_2Cl_2 (20 mL). *O*-(2,4,6- Trimethylbenzenesulfonyl)hydroxylamine (1.03 g, 4.8 mmol) was added to the solution, and the mixture was stirred for 2 h. This step prepares a substituted 1-aminopyridine. To another 100 mL round bottomed flask were added 5-bromofuran-3-carboxylic acid (0.76 g, 4 mmol), CH_2Cl_2 (20 mL), oxalyl chloride (8 mmol, 0.69 mL), and DMF (4 drops). The mixture was refluxed for two hours and cooled to room temperature. After removal of excess of oxalyl chloride and CH_2Cl_2, the residue was dissolved in CH_2Cl_2 (20 mL). To this solution were added the aminopyridinium solution prepared above and triethylamine (1.67 mL, 12 mmol) at room temperature. After stirring the mixture for 24 h, NaOH (50 mL of a 1 N aqueous solution) was poured in and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The extracts were dried over $MgSO_4$, and the residue was purified by column chromatography (gradient elution, EtOAc/MeOH, 0% → 10%) to give the product (0.52 g, 40%). Appearance: white solid; mp 206−207 °C (EtOAc/MeOH = 10:1); R_f = 0.48 (EtOAc/MeOH = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 7.0 Hz, 2H), 7.94 (s, 1H), 7.62 (d, J = 7.0 Hz, 2H), 6.73 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.2, 145.7, 142.6, 128.0, 123.2, 122.1, 111.6, 35.8, 30.3. HRMS (ESI) calcd for $C_{14}H_{15}BrN_2O_2$ $[M + H]^+$ 323.0390, found 323.0388.



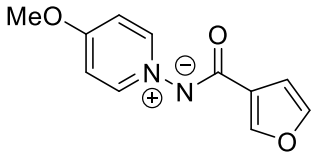
(2-Bromoisonicotinoyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide

Method B was employed, with 2-bromoisonicotinic acid (4 mmol, 0.81 g). Yield : 0.68 g, 51%; appearance : white solid; mp 176−177 °C (EtOAc/MeOH = 10:1); R_f = 0.48 (EtOAc/MeOH = 10/1); purification (gradient elution, EtOAc/MeOH, 0% → 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 7.2 Hz, 2H), 8.42 (d, J = 5.3 Hz, 1H), 8.21 – 8.13 (m, 1H), 7.93 (dd, J = 5.1, 1.4 Hz, 1H), 7.68 (d, J = 7.1 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 163.9, 150.2, 148.3, 142.4, 142.3, 126.9, 123.4, 121.6, 35.9, 30.3. HRMS (ESI) calcd for $C_{15}H_{16}BrN_3O$ $[M + H]^+$ 334.0550, found 334.0550.



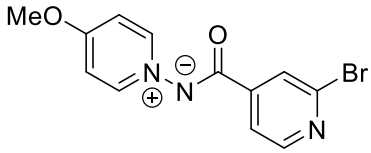
(Furan-2-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide

Method A was employed, with furan-2-carboxylic acid (0.45 g, 4 mmol). Yield: 0.47 g, 54%; Appearance: white solid; mp 187−188 °C (EtOAc/MeOH = 10:1); R_f = 0.12 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 7.6 Hz, 2H), 7.51 – 7.42 (m, 1H), 7.10 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 3.3 Hz, 1H), 6.46 (dd, J = 3.3, 1.7 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 164.3, 151.5, 144.9, 143.3, 112.4, 111.5, 111.1, 57.0. HRMS (ESI) calcd for $C_{11}H_{10}N_2O_3$ $[M + Na]^+$ 241.0584, found 241.0590.



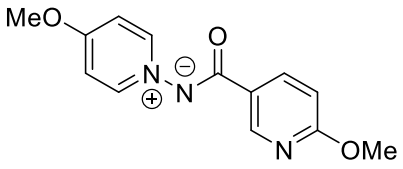
(Furan-3-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide

Method A was employed, with furan-3-carboxylic acid (0.45 g, 4 mmol). Yield: 0.43 g, 49%; Appearance: pale yellow solid; mp 127−128 °C (EtOAc/MeOH = 10:1); R_f = 0.21 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 7.3 Hz, 2H), 7.98 (s, 1H), 7.41 (s, 1H), 7.08 (d, J = 7.3 Hz, 2H), 6.80 (s, 1H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 166.1, 145.1, 144.5, 142.8, 125.2, 111.5, 109.8, 57.0. HRMS (ESI) calcd for $C_{11}H_{10}N_2O_3$ $[M + Na]^+$ 241.0584, found 241.0585.



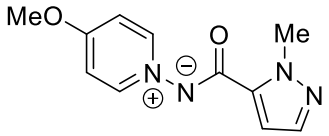
(2-Bromoisonicotinoyl)(4-methoxypyridin-1-ium-1-yl)amide

Method B was employed, with 2-bromoisonicotinic acid (0.81 g, 4 mmol). Yield: 0.55 g, 45%; Appearance: white solid; mp 192−193 °C (EtOAc/MeOH = 10:1); R_f = 0.21 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 7.2 Hz, 2H), 8.41 (d, J = 4.9 Hz, 1H), 8.16 (s, 1H), 7.92 (d, J = 4.9 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.5, 150.1, 148.4, 144.6, 142.4, 126.9, 121.5, 111.7, 57.1. HRMS (ESI) calcd for $C_{12}H_{10}N_3O_2Br$ $[M + Na]^+$ 329.9849, found 329.9849.



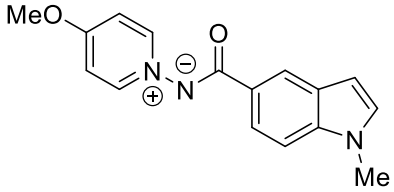
(6-Methoxynicotinoyl)(4-methoxypyridin-1-ium-1-yl)amide

Method A was employed, with 6-methoxynicotinic acid (0.61 g, 4 mmol). Yield: 0.47 g, 45%; Appearance: white solid; mp 176−177 °C (EtOAc/MeOH = 10:1); R_f = 0.18 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 1.8 Hz, 1H), 8.53 (d, J = 7.4 Hz, 2H), 8.28 (dd, J = 8.6, 1.8 Hz, 1H), 7.09 (d, J = 7.4 Hz, 2H), 6.73 (d, J = 8.6 Hz, 1H), 4.01 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 166.1, 165.3, 147.7, 145.1, 138.5, 126.4, 111.5, 109.8, 57.0, 53.7. HRMS (ESI) calcd for $C_{13}H_{13}N_3O_3$ $[M + Na]^+$ 282.0849, found 282.0847.



(4-Methoxypyridin-1-ium-1-yl)(1-methyl-1H-pyrazole-5-carbonyl)amide

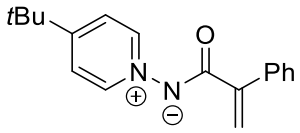
Method A was employed, with 1-methyl-1H-pyrazole-5-carboxylic acid (0.50 g, 4 mmol). Yield: 0.55 g, 59%; Appearance: white solid; mp 148− 149 °C (EtOAc/MeOH = 10:1); R_f = 0.15 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 1.8 Hz, 1H), 7.10 (d, J = 7.6 Hz, 2H), 6.73 (d, J = 1.8 Hz, 1H), 4.23 (s, 3H), 4.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 165.8, 145.0, 138.7, 137.5, 111.6, 107.4, 57.1, 39.4. HRMS (ESI) calcd for $C_{11}H_{12}N_4O_2$ $[M + Na]^+$ 255.0852, found 255.0858.



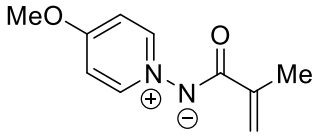
(4-Methoxypyridin-1-ium-1-yl)(1-methyl-1H-indole-5-carbonyl)amide

Method A was employed, with 1-methyl-1H-indole-5-carboxylic acid (0.70 g, 4 mmol). Yield: 0.75 g, 67%; Appearance: white solid; mp 219− 220 °C (EtOAc/MeOH = 10:1); R_f = 0.21 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 20%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.62 (d, J = 6.1 Hz, 2H), 8.25 (s, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.47 – 7.26 (m, 4H), 6.47 (s, 1H), 4.01 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.1, 165.4, 145.1, 137.3, 129.9, 129.1, 127.3, 121.4, 120.3, 111.8, 108.2, 101.2, 57.1, 32.6. HRMS (ESI) calcd for $C_{16}H_{15}N_3O_2$ $[M + Na]^+$ 304.1056, found 304.1056.

Preparation of pyridinium ylides (Method C)



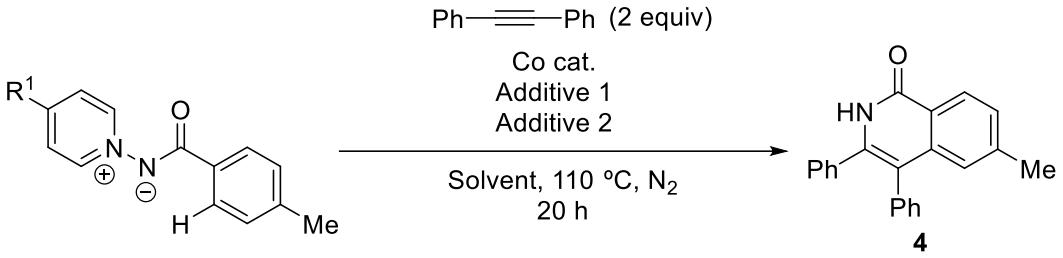
(4-(tert-Butyl)pyridin-1-ium-1-yl)(2-phenylacryloyl)amide. To a 100 mL round bottomed flask were added 4-tert-butylpyridine (0.59 mL, 4 mmol) and CH_2Cl_2 (20 mL). *O*-(2,4,6-Trimethylbenzenesulfonyl)hydroxylamine (1.03 g, 4.8 mmol) was added to the solution, and the mixture was stirred for 2 h. This step prepares a substituted 1-aminopyridine. To another 100 mL round bottomed flask were added atropic acid (0.59 g, 4 mmol) and CH_2Cl_2 (20 mL), and the mixture was cooled to 0 °C. Ethyl chloroformate (0.42 mL, 4.4 mmol) was added to the mixture followed by the addition of triethylamine (1.67 mL, 12 mmol). The mixture was stirred for 30 min at room temperature. To this mixture were added the 1-aminopyridinium solution prepared above dropwise, solid K_2CO_3 (1.66 g, 12 mmol) and acetonitrile (20 mL). After stirring the mixture for 24 h, NaOH (50 mL of a 1 N aqueous solution) was poured in and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The extracts were dried over $MgSO_4$, and the residue was purified by column chromatography (gradient elution, EtOAc/MeOH, 0% → 10%) to give the product (0.42 g, 37%). Appearance: pale yellow solid; mp 146−147 °C (EtOAc/MeOH = 10:1); R_f = 0.50 (EtOAc/MeOH = 8/2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, J = 7.2 Hz, 2H), 7.66 – 7.52 (m, 4H), 7.33 (d, J = 7.3 Hz, 2H), 7.30 – 7.22 (m, 1H), 6.11 (d, J = 1.8 Hz, 1H), 5.61 (d, J = 1.8 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 163.0, 147.7, 142.6, 139.4, 128.3, 127.9, 127.3, 123.0, 119.2, 35.7, 30.3. HRMS (ESI) calcd for $C_{18}H_{20}N_2O$ $[M + H]^+$ 281.1651, found 281.1648.



Methacryloyl(4-methoxypyridin-1-ium-1-yl)amide. Method C was employed, with methacrylic acid (0.34 g, 4 mmol). Yield: 0.60 g, 78%; Appearance: pale yellow solid; mp 85−86 °C (EtOAc/MeOH = 10:1); R_f = 0.16 (EtOAc/MeOH = 8/2); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.1 Hz, 2H), 7.04 (d, J = 7.1 Hz, 2H), 5.96 (s, 1H), 5.24 (s, 1H), 3.98 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz $CDCl_3$) δ 173.0, 166.1, 145.1, 142.4, 118.5, 111.4, 56.9, 19.4. HRMS (ESI) calcd for $C_{10}H_{12}N_2O_2$ $[M + H]^+$ 193.0972, found 193.0975.

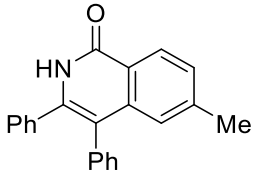
General Procedure for Cobalt-Catalyzed C−H Annulation. A 2-dram vial equipped with a magnetic stir bar was charged with the pyridinium ylide (0.2 mmol), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 or 0.04 mmol), pivalic acid (0.04 or 0.06 mmol), HFIP (1 mL), and alkyne (0.4 mmol). The vial was closed with a screw cap after flushing with nitrogen. The mixture was stirred in a heating block at 110 °C for 20−72 h. After the mixture was cooled, ethyl acetate was added, and the diluted mixture was poured into a round bottom flask. The mixture was absorbed on 3 g of silica gel and purified by column chromatography on silica gel.

Optimization Study[a]



Entry	R	Cat.	Additive 1	Additive 2	Solvent	Yield (%)[b]
1	H	$Cp^*CoI_2(CO)$ 5 mol%	$AgSbF_6$ (20 mol%)	NaOAc (40 mol%)	TFE	8
2	*t*Bu	$Cp^*CoI_2(CO)$ 10 mol%	$AgSbF_6$ (20 mol%)	NaOAc (40 mol%)	HFIP	30
3	*t*Bu	$Cp^*CoI_2(CO)$ 20 mol%	$AgSbF_6$ (40 mol%)	PivOH (20 mol%)	HFIP	60
4	*t*Bu	$[Cp^*Co(MeCN)_3][SbF_6]_2$ 15 mol%		NaOAc (40 mol%)	TFE	45
5	*t*Bu	$[Cp^*Co(MeCN)_3][SbF_6]_2$ 15 mol%		1-$AdCO_2H$ (20 mol%)	HFIP	77
6	***t*Bu**	**$[Cp^*Co(MeCN)_3][SbF_6]_2$ 15 mol%**		**PivOH (20 mol%)**	**HFIP**	**81**
7	*t*Bu	$[CpCo(MeCN)_3][SbF_6]_2$ 15 mol%		PivOH (20 mol%)	HFIP	**7**
8	*t*Bu	$[Cp^*Co(MeCN)_3][SbF_6]_2$ 15 mol%			HFIP	55
9	**OMe**	**$[Cp^*Co(MeCN)_3][SbF_6]_2$ 15 mol%**		**PivOH (20 mol%)**	**HFIP**	**82**
10	H	$[Cp^*Co(MeCN)_3][SbF_6]_2$ 15 mol%		PivOH (20 mol%)	HFIP	24

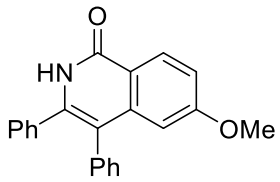
[a] Reaction conditions: ylide (0.2 mmol), HFIP (1 mL). [b] Isolated yields.



6-Methyl-3,4-diphenylisoquinolin-1(*2H*)-one (4). Ylide **3** (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h;

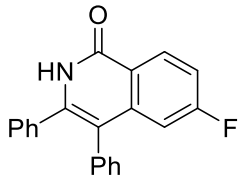
white solid; 81% yield (50 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.50 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.35 (d, J = 8.1 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.26 – 7.21 (m, 5H), 7.21 – 7.21 (m, 2H), 7.12 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 143.4, 138.9, 137.4, 136.1, 135.3, 132.0, 129.5, 128.6, 128.5, 128.4, 128.3, 127.6, 127.3, 125.4, 123.1, 117.1, 22.2. This compound is known.[3]

Ylide **2** (0.2 mmol, 48 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg). 20 h; 82% yield (51 mg).



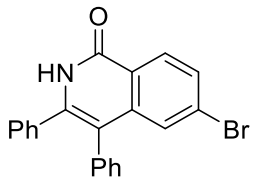
6-Methoxy-3,4-diphenylisoquinolin-1(*2H*)-one (5). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-methoxybenzoyl)-amide (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 64% yield (42 mg); purification (gradient elution, hexanes/EtOAc, 40% → 100%); R_f = 0.30 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.38 (s, 1H), 8.25 (d, J = 8.8 Hz, 1H), 7.36 – 7.18 (m, 8H), 7.18 – 7.09 (m, 3H), 6.51 (d, J = 2.4 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.3, 161.4, 140.2, 139.3, 135.9, 134.6, 131.7, 129.8, 129.2, 128.3, 128.2, 127.7, 127.1, 118.9, 115.1, 114.6, 107.2, 55.2. This compound is known.[4]

(4-Methoxybenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 52 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; 76% yield (50 mg).

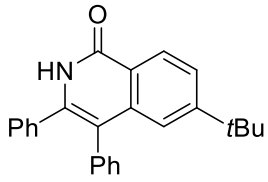


6-Fluoro-3,4-diphenylisoquinolin-1(*2H*)-one (6). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-fluorobenzoyl)amide (0.2 mmol, 57 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 63% yield (40 mg); purification (gradient elution, hexanes/EtOAc, 30% → 50%); R_f = 0.53 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.45 (dd, J = 8.9, 6.0 Hz, 1H), 7.37 – 7.22 (m, 8H), 7.21 – 7.14 (m, 3H), 6.98 (dd, J = 10.7, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, J = 252.2 Hz), 162.4, 141.4 (d, J = 10.0 Hz), 138.8, 135.4, 134.8, 131.8, 130.8 (d, J = 10.0 Hz), 129.4, 129.0, 128.7, 128.5, 127.7, 121.9 (d, J = 1.6 Hz), 116.9 (d, J = 3.3 Hz), 115.3 (d, J = 23.6 Hz), 111.0 (d, J = 23.4 Hz). This compound is known.[3]

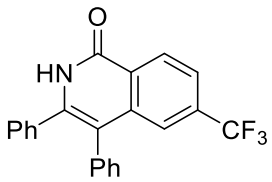
(4-Fluorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 49 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; 78% yield (49 mg).



6-Bromo-3,4-diphenylisoquinolin-1(2H)-one (7). (4-Bromobenzoyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide (0.2 mmol, 67 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 76% yield (57 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.67 (hexanes/EtOAc = 1/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.76 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.68 (dd, J = 8.5, 1.8 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.26 – 7.19 (m, 6H), 7.18 – 7.13 (m, 2H). ^{13}C NMR (151 MHz, DMSO-D_6) δ 161.3, 140.3, 139.9, 135.2, 134.2, 131.7, 129.8, 129.4, 129.30, 128.5, 127.8, 127.5, 127.0, 126.9, 123.9, 114.5. One carbon signal could not be located. This compound is known.[3]

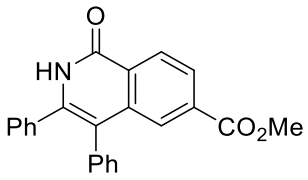


6-(tert-Butyl)-3,4-diphenylisoquinolin-1(*2H*)-one (8). (4-(tert-Butyl)benzoyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide (0.2 mmol, 62 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 64% yield (45 mg); purification (gradient elution, hexanes/EtOAc, 20% → 50%); R_f = 0.63 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.40 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.39 – 7.13 (m, 11H), 1.25 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 156.3, 138.7, 137.1, 136.0, 135.4, 132.0, 129.4, 128.7, 128.5, 128.4, 127.4, 124.9, 123.0, 121.9, 117.7, 35.4, 31.1. One carbon signal could not be located. This compound is known.[6]

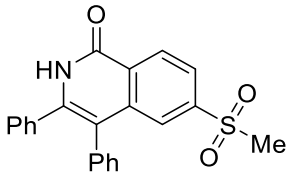


3,4-Diphenyl-6-(trifluoromethyl)isoquinolin-1(*2H*)-one (9). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-(trifluoromethyl)benzoyl)amide (0.2 mmol, 64 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; white solid; 70% yield (51 mg); purification (gradient elution, hexanes/EtOAc, 20% → 40%); R_f = 0.73 (hexanes/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.53 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.63 (s, 1H), 7.39 – 7.22 (m, 8H), 7.17 (d, J = 5.8

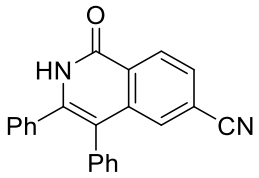
Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 139.1, 138.9, 134.9, 134.6, 134.4 (q, J = 32.4 Hz), 131.8, 129.5, 129.1, 128.8, 128.7, 128.5, 127.9, 127.3, 123.8 (q, J = 272.9 Hz), 123.0 (q, J = 4.0 Hz), 122.6 (q, J = 3.4 Hz), 117.2. This compound is known.[3]



Methyl 1-oxo-3,4-diphenyl-1,2-dihydroisoquinoline-6-carboxylate (10). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-(methoxycarbonyl)benzoyl)amide (0.2 mmol, 62 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; pale yellow solid; 75% yield (53 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.53 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.80 (s, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.79 (s, 1H), 7.36 – 7.27 (m, 3H), 7.27 – 7.20 (m, 5H), 7.19 – 7.13 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.7, 161.2, 139.8, 138.1, 135.3, 134.3, 132.8, 131.7, 129.8, 128.4, 127.8, 127.7, 127.7, 127.4, 126.3, 125.8, 115.5, 52.6. One carbon signal could not be located. This compound is known.[6]



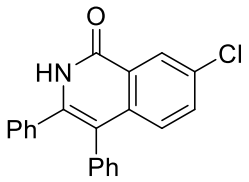
6-(Methylsulfonyl)-3,4-diphenylisoquinolin-1(2H)-one (11). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-(methylsulfonyl)benzoyl)amide (0.2 mmol, 66 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; mp 326−327 °C (CH_2Cl_2); 72% yield (54 mg); purification (gradient elution, hexanes/EtOAc, 30% → 100%); R_f = 0.25 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.70 (s, 1H), 7.38 – 7.29 (m, 3H), 7.28 – 7.22 (m, 5H), 7.22 – 7.15 (m, 2H), 3.23 (s, 3H). ^{13}C NMR (126 MHz, DMSO-D_6) δ 161.0, 144.1, 140.8, 138.3, 134.9, 134.1, 131.8, 129.9, 128.8, 128.6, 128.5, 127.8, 127.6, 123.8, 123.6, 115.4, 43.2. One carbon signal could not be located. HRMS (ESI) calcd for $C_{22}H_{17}NO_3S$ $[M + H]^+$ 376.1002, found 376.1001.



1-Oxo-3,4-diphenyl-1,2-dihydroisoquinoline-6-carbonitrile (12). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-cyanobenzoyl)amide (0.2 mmol, 56 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; pale orange solid; 51% yield (33 mg); purification

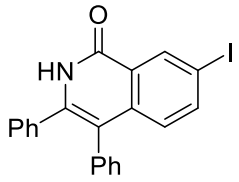
(gradient elution, hexanes/EtOAc, 30% → 100%); R_f = 0.56 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H), 8.43 (d, J = 8.3 Hz, 1H), 7.87 (dd, J = 8.2, 1.5 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.37 – 7.20 (m, 8H), 7.19 – 7.11 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.9, 140.8, 138.2, 134.7, 134.0, 131.7, 129.9, 129.5, 128.7, 128.6, 128.3, 128.1, 127.8, 127.6, 127.5, 118.4, 115.0, 114.6. This compound is known.[3]

(4-Cyanobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 51 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 76% yield (40 mg).



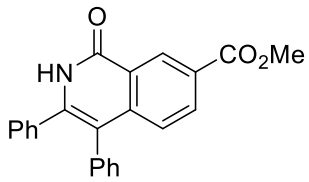
7-Chloro-3,4-diphenylisoquinolin-1(2H)-one (13). (4-(tert-Butyl)pyridin-1-ium-1-yl)(3-chlorobenzoyl)amide (0.2 mmol, 58 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; pale yellow solid; 54% yield (36 mg); purification (gradient elution, hexanes/EtOAc, 30% → 70%); R_f = 0.75 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 8.24 (d, J = 2.3 Hz, 1H), 7.69 (dd, J = 8.8, 2.3 Hz, 1H), 7.35 – 7.20 (m, 8H), 7.19 – 7.12 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.7, 149.5, 139.2, 136.8, 135.4, 134.2, 132.7, 131.7, 131.0, 129.8, 128.4, 127.7, 127.4, 127.3, 126.2, 125.8, 115.1. One carbon signal could not be located. This compound is known.[3]

(3-Chlorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 53 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; 63% yield (42 mg).

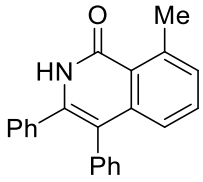


7-Iodo-3,4-diphenylisoquinolin-1(2H)-one (14). (4-(tert-Butyl)pyridin-1-ium-1-yl)(3-iodobenzoyl)amide (0.2 mmol, 76 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg); 48 h; pale yellow solid; mp 266−267 °C (CH_2Cl_2); 48% yield (41 mg); purification (gradient elution, hexanes/EtOAc, 30% → 70%); R_f = 0.75 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 8.59 (d, J = 1.9 Hz, 1H), 7.95 (dd, J = 8.6, 2.0 Hz, 1H), 7.35 – 7.19 (m, 8H), 7.16 – 7.09 (m, 2H), 6.93 (d, J = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.4, 140.8, 139.4, 137.3, 135.3, 135.1, 134.3, 131.7, 129.8, 128.5, 128.4, 127.7, 127.2, 127.2, 126.6, 115.2, 91.8. HRMS (ESI) calcd for $C_{21}H_{14}INO$ $[M + H]^+$ 424.0193, found 424.0194.

(3-Iodobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 71 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; 63% yield (53 mg).

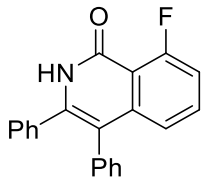


Methyl 1-oxo-3,4-diphenyl-1,2-dihydroisoquinoline-7-carboxylate (15). (4-(tert-Butyl)pyridin-1-ium-1-yl)(3-(methoxycarbonyl)benzoyl)amide (0.2 mmol, 62 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; white solid; mp 254−255 °C (CH_2Cl_2); 66% yield (47 mg); purification (gradient elution, hexanes/EtOAc, 30% → 90%); R_f = 0.63 (hexanes/EtOAc = 1/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.86 (s, 1H), 8.88 (s, 1H), 8.20 – 8.02 (m, 1H), 7.35 – 7.20 (m, 9H), 7.19 – 7.12 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.7, 161.5, 141.5, 135.4, 134.2, 132.1, 131.7, 129.8, 128.7, 128.6, 128.4, 127.8, 127.3, 126.8, 125.6, 124.7, 115.4, 52.4. HRMS (ESI) calcd for $C_{23}H_{17}NO_3$ $[M + H]^+$ 356.1281, found 356.1284.



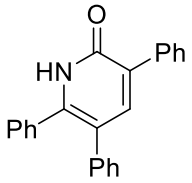
8-Methyl-3,4-diphenylisoquinolin-1(2H)-one (16). (4-(tert-Butyl)pyridin-1-ium-1-yl)(2-methylbenzoyl)-amide (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 38% yield (24 mg); purification (gradient elution, hexanes/EtOAc, 20% → 50%); R_f = 0.87 (hexanes/EtOAc = 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.41 – 7.35 (m, 1H), 7.33 – 7.19 (m, 9H), 7.18 – 7.14 (m, 3H), 2.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 142.0, 140.6, 137.5, 136.7, 135.1, 132.1, 131.8, 129.7, 129.5, 128.5, 128.5, 128.3, 127.3, 124.0, 123.7, 117.3, 24.0. This compound is known.[3]

(4-Methoxypyridin-1-ium-1-yl)(2-methylbenzoyl)amide (0.2 mmol, 48 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 54% yield (34 mg).

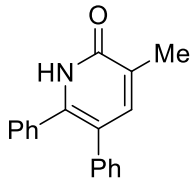


8-Fluoro-3,4-diphenylisoquinolin-1(2H)-one (17). (4-(tert-Butyl)pyridin-1-ium-1-yl)(2-fluorobenzoyl)amide (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; white solid; 51% yield (32 mg); purification (gradient elution, hexanes/EtOAc, 20% → 50%); R_f = 0.66 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.48 (td, J = 8.1, 5.1 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.27 – 7.21 (m, 5H), 7.20 – 7.15 (m, 2H), 7.14 – 7.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J = 264.0 Hz), 160.5, 141.7, 138.6, 135.8, 134.6, 133.4 (d, J = 10.2 Hz), 132.0, 129.3, 129.0, 128.6, 128.5, 127.6, 121.7 (d, J = 4.4 Hz), 116.5, 114.5 (d, J = 6.1 Hz), 113.5 (d, J = 21.6 Hz). This compound is known.[4]

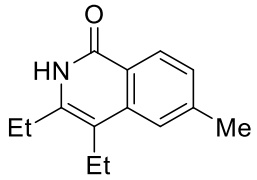
(2-Fluorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 49 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 71% yield (45 mg).



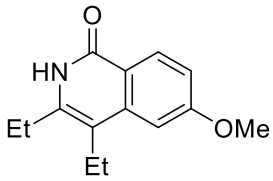
3,5,6-Triphenylpyridin-2(1H)-one (18). (4-(tert-butyl)pyridin-1-ium-1-yl)(2-phenylacryloyl)amide (0.2 mmol, 56 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; white solid; 65% yield (42 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); Appearance: white solid. R_f = 0.60 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.06 (s, 1H), 7.83 (d, J = 7.4 Hz, 2H), 7.69 (s, 1H), 7.46 – 7.16 (m, 11H), 7.15 – 7.07 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 125.3, 105.6, 104.8, 100.4, 98.4, 96.0, 92.2, 92.1, 91.7, 90.9, 90.9, 90.6, 90.2, 89.4, 82.0, 39.7, 39.5, 39.3. Two carbon signals could not be located. This compound is known.[5]



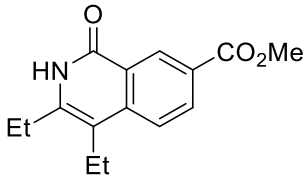
3-Methyl-5,6-diphenylpyridin-2(1H)-one (19). Methacryloyl(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 38 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; white solid; 82% yield (43 mg); purification (gradient elution, hexanes/EtOAc, 20% → 90%); R_f = 0.20 (hexanes/EtOAc = 1/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.47 – 7.39 (m, 1H), 7.35 – 7.15 (m, 8H), 7.13 – 7.03 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 142.0, 140.9, 138.1, 134.1, 129.7, 129.5, 129.2, 128.6, 128.4, 128.4, 126.9, 118.9, 16.4. This compound is known.[5]



3,4-Diethyl-6-methylisoquinolin-1(2H)-one (20). Ylide **3** (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 20 h; white solid; mp 212−213 °C (CH_2Cl_2); 70% yield (30 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.55 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 8.35 (d, J = 8.2 Hz, 1H), 7.46 (s, 1H), 7.36 – 7.16 (m, 1H), 2.83 – 2.63 (m, 4H), 1.33 (t, J = 7.6 Hz, 3H), 1.21 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 142.9, 139.3, 138.5, 127.9, 127.0, 123.1, 122.8, 113.7, 24.4, 22.4, 19.6, 15.1, 14.1. HRMS (ESI) calcd for $C_{14}H_{17}NO$ $[M + H]^+$ 216.1383, found 232.1387.



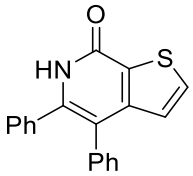
3,4-Diethyl-6-methoxyisoquinolin-1(2H)-one (21). (4-(tert-Butyl)pyridin-1-ium-1-yl)(4-methoxybenzoyl)-amide (0.2 mmol, 57 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL). 48 h; light tan solid; mp 167−168 °C (CH_2Cl_2); 69% yield (32 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.39 (hexanes/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 8.37 (d, J = 8.5 Hz, 1H), 7.10 – 6.94 (m, 2H), 3.93 (s, 3H), 2.76 – 2.62 (m, 4H), 1.30 (t, J = 7.4 Hz, 3H), 1.20 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 163.0, 140.4, 140.0, 129.9, 119.1, 114.1, 113.6, 104.9, 55.5, 24.5, 19.8, 14.8, 14.1. HRMS (ESI) calcd for $C_{14}H_{17}NO_2$ $[M + H]^+$ 232.1332, found 232.1334.



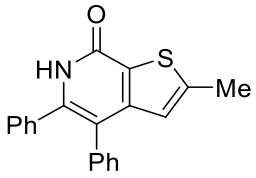
Methyl 3,4-diethyl-1-oxo-1,2-dihydroisoquinoline-7-carboxylate (22). (4-(tert-Butyl)pyridin-1-ium-1-yl)(3-(methoxycarbonyl)benzoyl)amide (0.2 mmol, 62 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 72 h; light tan solid; mp 211−212 °C (CH_2Cl_2); 52% yield (27 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.50 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 9.12 (s, 1H), 8.29 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 3.99 (s, 3H), 2.79 (q, J = 7.2 Hz, 4H), 1.39 (t, J = 7.5 Hz, 3H), 1.22 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

166.8, 164.0, 142.6, 141.7, 132.6, 130.2, 126.8, 124.8, 123.2, 114.1, 52.4, 24.6, 19.7, 15.0, 14.2. HRMS (ESI) calcd for $C_{15}H_{17}NO_3$ $[M + H]^+$ 260.1281, found 260.1279.

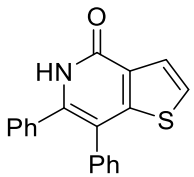
(3-(Methoxycarbonyl)benzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 57 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 48 h; 66% yield (34 mg).



4,5-Diphenylthieno[2,3-c]pyridin-7(6H)-one (23). (4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-2-carbonyl)-amide (0.2 mmol, 52 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 82% yield (50 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.59 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.68 (d, J = 5.2 Hz, 1H), 7.37 – 7.22 (m, 8H), 7.21 – 7.15 (m, 2H), 7.07 (d, J = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 146.8, 139.9, 136.4, 134.2, 134.0, 130.8, 130.1, 128.4, 128.3, 128.1, 127.9, 127.0, 124.6, 114.8. This compound is known.[7]

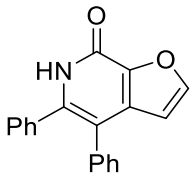


2-Methyl-4,5-diphenylthieno[2,3-c]pyridin-7(6H)-one (24). (4-(tert-Butyl)pyridin-1-ium-1-yl)(5-methylthio-phene-2-carbonyl)amide (0.2 mmol, 55 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; mp 287−288 °C (CH_2Cl_2); 79% yield (50 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.54 (hexanes/EtOAc = 1/1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.70 (s, 1H), 7.30 – 7.17 (m, 8H), 7.15 – 7.07 (m, 2H), 6.64 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.7, 148.2, 147.3, 140.0, 136.5, 134.0, 130.8, 130.1, 128.4, 128.3, 127.8, 127.0, 126.5, 123.0, 114.5, 15.9. HRMS (ESI) calcd for $C_{20}H_{15}NOS$ $[M + H]^+$ 318.0947, found 318.0948.



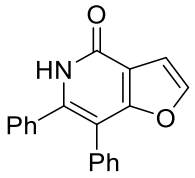
6,7-Diphenylthieno[3,2-c]pyridin-4(5H)-one (25). (4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-3-carbonyl)-amide (0.2 mmol, 55 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 20 h; white solid; 82% yield (50 mg); purification (gradient elution,

hexanes/EtOAc, 30% → 80%); R_f = 0.44 (hexanes/EtOAc = 1/1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.68 – 7.49 (m, 2H), 7.37 – 7.13 (m, 10H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.1, 151.8, 139.2, 137.0, 134.0, 130.7, 130.5, 129.8, 129.1, 128.4, 128.2, 126.4, 125.1, 114.2. One carbon signal could not be located. This compound is known.[8]



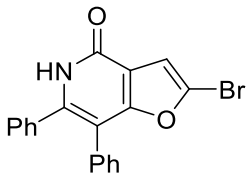
4,5-Diphenylfuro[2,3-c]pyridin-7(6H)-one (26). (4-(tert-Butyl)pyridin-1-ium-1-yl)(furan-2-carbonyl)amide (0.2 mmol, 49 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; pale brown solid; 24% yield (14 mg); purification (gradient elution, hexanes/EtOAc, 30% → 80%); R_f = 0.29 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.59 (d, J = 1.8 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.19 – 7.08 (m, 5H), 7.07 – 6.99 (m, 2H), 6.50 (d, J = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 149.1, 141.9, 138.3, 136.4, 135.3, 134.0, 130.3, 129.6, 128.9, 128.6, 128.4, 127.5, 114.4, 107.5. This compound is known.[9]

(Furan-2-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 44 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 23% yield (13 mg).

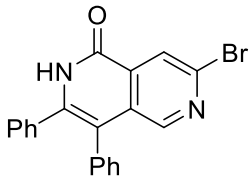


6,7-Diphenylfuro[3,2-c]pyridin-4(5H)-one (27). (4-(tert-butyl)pyridin-1-ium-1-yl)(furan-3-carbonyl)amide (0.2 mmol, 49 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; 65% yield (37 mg); purification (gradient elution, hexanes/EtOAc, 30% → 80%); R_f = 0.27 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 7.89 (s, 1H), 7.38 – 7.22 (m, 8H), 7.21 – 7.14 (m, 2H), 7.04 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.1, 158.8, 144.6, 140.8, 133.3, 132.4, 130.8, 130.1, 128.8, 128.2, 128.0, 127.2, 114.5, 108.0, 107.1. This compound is known.[7]

(Furan-3-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 44 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 56% yield (32 mg).

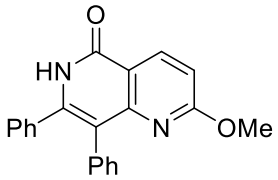


2-Bromo-6,7-diphenylfuro[3,2-c]pyridin-4(5H)-one (28). (5-Bromofuran-3-carbonyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide (0.2 mmol, 65 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; mp 287−288 °C (CH_2Cl_2); 70% yield (51 mg); purification (gradient elution, hexanes/EtOAc, 30% → 70%); R_f = 0.34 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.85 (d, *J* = 4.3 Hz, 1H), 7.38 – 7.01 (m, 11H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 160.1, 157.5, 141.4, 133.0, 131.8, 130.8, 130.0, 128.9, 128.3, 128.0, 127.5, 125.0, 116.1, 109.0, 107.5. HRMS (ESI) calcd for $C_{19}H_{12}BrNO_2$ $[M + H]^+$ 366.0124, found 366.0126.



7-Bromo-3,4-diphenyl-2,6-naphthyridin-1(2H)-one (29). (2-Bromoisonicotinoyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide (0.2 mmol, 49 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; pale yellow solid; mp 261−262 °C (CH_2Cl_2); 30% yield (23 mg); purification (gradient elution, hexanes/EtOAc, 20% → 60%); R_f = 0.78 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 8.53 (s, 1H), 8.30 (s, 1H), 7.39 – 7.23 (m, 8H), 7.22 – 7.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 150.2, 139.5, 138.4, 133.9, 133.6, 132.1, 132.0, 131.6, 129.4, 129.4, 128.9, 128.6, 128.2, 123.8, 115.3. HRMS (ESI) calcd for $C_{20}H_{13}BrN_2O$ $[M + H]^+$ 377.0284, found 377.0283.

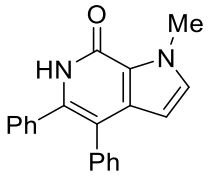
(2-Bromoisonicotinoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 62 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; 70% yield (53 mg).



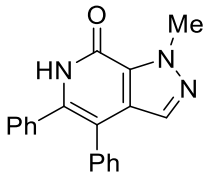
2-Methoxy-7,8-diphenyl-1,6-naphthyridin-5(6H)-one (30). (4-(tert-Butyl)pyridin-1-ium-1-yl)(6-methoxynicotinoyl)amide (0.2 mmol, 57 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.04 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; white solid; mp 264−265 °C (CH_2Cl_2); 58% yield (38 mg); purification (gradient elution, hexanes/EtOAc, 30% → 70%); R_f = 0.56 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.46 (d, *J* = 8.7 Hz, 1H), 7.35 – 7.17 (m, 10H), 6.80 (d, *J* = 8.7 Hz, 1H), 3.76

(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 162.8, 153.6, 142.0, 138.2, 135.1, 134.9, 132.4, 129.7, 129.1, 128.5, 127.4, 126.7, 118.4, 115.8, 111.0, 53.8. HRMS (ESI) calcd for $C_{21}H_{16}N_2O_2$ $[M + H]^+$ 329.1285, found 329.1286.

(6-Methoxynicotinoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 52 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; 53% yield (35 mg).

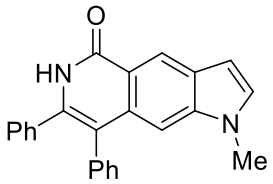


1-Methyl-4,5-diphenyl-1,6-dihydro-7H-pyrrolo[2,3-c]pyridin-7-one (31). (4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-pyrrole-2-carbonyl)amide (0.2 mmol, 51 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; light tan solid; mp 277−278 °C (CH_2Cl_2); 68% yield (41 mg); purification (gradient elution, hexanes/EtOAc, 30% → 80%); R_f = 0.32 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.06 (s, 1H), 7.30 (d, J = 2.7 Hz, 1H), 7.27 – 7.13 (m, 8H), 7.12 – 7.05 (m, 2H), 5.96 (d, J = 2.7 Hz, 1H), 4.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.4, 136.8, 134.7, 134.2, 132.6, 132.1, 130.4, 130.2, 128.1, 127.8, 126.5, 121.6, 113.2, 101.6, 35.3. HRMS (ESI) calcd for $C_{20}H_{16}N_2O$ $[M + H]^+$ 301.1335, found 301.1340.



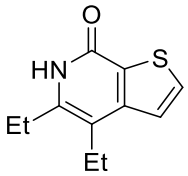
1-Methyl-4,5-diphenyl-1,6-dihydro-7H-pyrazolo[3,4-c]pyridin-7-one (32). (4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-pyrazole-5-carbonyl)amide (0.2 mmol, 52 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; white solid; mp 243−244 °C (CH_2Cl_2); 35% yield (21 mg); purification (gradient elution, hexanes/EtOAc, 30% → 70%); R_f = 0.56 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.64 (s, 1H), 7.35 – 7.23 (m, 8H), 7.22 – 7.14 (m, 2H), 4.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 135.7, 134.5, 134.5, 133.5, 130.4, 129.8, 129.4, 128.9, 128.7, 128.6, 128.5, 127.4, 113.1, 38.5. HRMS (ESI) calcd for $C_{19}H_{15}N_3O$ $[M + H]^+$ 302.1288, found 302.1292.

(4-Methoxypyridin-1-ium-1-yl)(1-methyl-1H-pyrazole-5-carbonyl)amide (0.2 mmol, 46 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 72 h; 71% yield (43 mg).

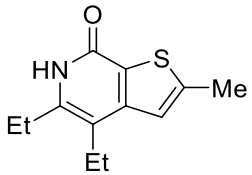


1-Methyl-7,8-diphenyl-1,6-dihydro-5H-pyrrolo[2,3-g]isoquinolin-5-one (33). (4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-indole-5-carbonyl)amide (0.2 mmol, 61 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; pale yellow solid; mp 332−333 °C (CH_2Cl_2); 51% yield (36 mg); purification (gradient elution, hexanes/EtOAc, 20% → 60%); R_f = 0.42 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (s, 1H), 8.62 (s, 1H), 7.54 (d, J = 3.1 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.25 – 7.14 (m, 7H), 7.00 (s, 1H), 6.67 (d, J = 3.1 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.7, 139.4, 136.8, 135.5, 135.3, 133.4, 132.6, 131.9, 129.9, 128.3, 128.0, 127.6, 127.6, 127.0, 119.7, 118.6, 116.0, 103.6, 101.3, 32.6. HRMS (ESI) calcd for $C_{24}H_{18}N_2O$ $[M + H]^+$ 351.1492, found 351.1499.

(4-Methoxypyridin-1-ium-1-yl)(1-methyl-1H-indole-5-carbonyl)amide (0.2 mmol, 56 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 58% yield (33 mg).

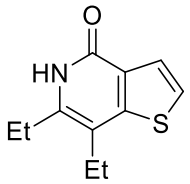


4,5-Diethylthieno[2,3-c]pyridin-7(6H)-one (34). (4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-2-carbonyl)amide amide (0.2 mmol, 52 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 48 h; pale brown solid; 72% yield (30 mg); purification (gradient elution, hexanes/EtOAc, 20% → 60%); R_f = 0.39 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 7.71 (d, J = 4.8 Hz, 1H), 7.45 – 7.21 (m, 1H), 2.93 – 2.53 (m, 4H), 1.33 (t, J = 7.0 Hz, 3H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 148.2, 141.3, 133.2, 127.4, 123.0, 114.6, 23.7, 21.5, 15.5, 14.7. This compound is known.[10]

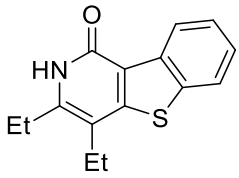


4,5-Diethyl-2-methylthieno[2,3-c]pyridin-7(6H)-one (35). (4-(tert-Butyl)pyridin-1-ium-1-yl)(5-methylthiophene-2-carbonyl)amide (0.2 mmol, 55 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 48 h; pale brown solid; mp 213−214 °C (CH_2Cl_2); 68% yield (30 mg); purification (gradient elution, hexanes/EtOAc, 20% → 60%); R_f = 0.37 (hexanes/EtOAc = 1/1); ^{1}H NMR

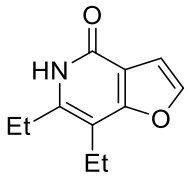
(400 MHz, $CDCl_3$) δ 11.40 (s, 1H), 6.93 (s, 1H), 2.74 – 2.62 (m, 4H), 2.61 (s, 3H), 1.28 (t, J = 7.5 Hz, 3H), 1.17 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 148.9, 148.6, 141.2, 126.0, 121.3, 114.3, 23.7, 21.4, 16.6, 15.4, 14.6. HRMS (ESI) calcd for $C_{12}H_{15}NOS$ $[M + H]^+$ 222.0947, found 222.0949.



6,7-Diethylthieno[3,2-c]pyridin-4(5H)-one (36). (4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-3-carbonyl)amide (0.2 mmol, 52 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 20 h; white solid; 72% yield (30 mg); purification (gradient elution, hexanes/EtOAc, 20% → 80%); R_f = 0.24 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 7.65 (d, J = 5.4 Hz, 1H), 7.27 – 7.20 (m, 1H), 2.77 – 2.60 (m, 4H), 1.32 (t, J = 7.6 Hz, 3H), 1.25 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 152.4, 140.3, 128.5, 125.1, 123.2, 113.9, 23.7, 23.1, 14.3, 14.3. This compound is known.[10]



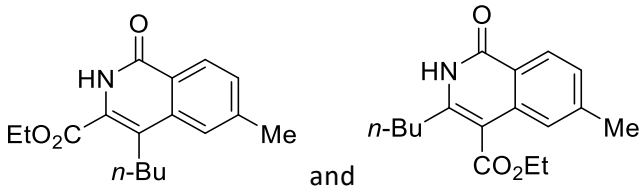
3,4-Diethylbenzo[4,5]thieno[3,2-c]pyridin-1(2H)-one (37). (4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-3-carbonyl)amide (0.2 mmol, 62 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 20 h; white solid; mp 229−230 °C (CH_2Cl_2); 87% yield (45 mg); purification (gradient elution, hexanes/EtOAc, 20% → 70%); R_f = 0.45 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 2.86 (q, J = 7.6 Hz, 2H), 2.73 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.6 Hz, 3H), 1.28 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 154.0, 143.4, 137.5, 137.3, 125.3, 125.3, 124.7, 121.9, 121.2, 114.1, 23.9, 23.1, 14.4, 14.4. HRMS (ESI) calcd for $C_{15}H_{15}NOS$ $[M + H]^+$ 258.0947, found 258.0948.



6,7-Diethylfuro[3,2-c]pyridin-4(5H)-one (38). (4-(tert-Butyl)pyridin-1-ium-1-yl)(furan-3-carbonyl)amide (0.2 mmol, 49 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL), 48 h; white solid; mp 150−151 °C (CH_2Cl_2); 18% yield (7 mg); purification (gradient

elution, hexanes/EtOAc, 20% → 80%); R_f = 0.21 (hexanes/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 7.48 (s, 1H), 6.95 (s, 1H), 2.77 – 2.60 (m, 4H), 1.29 (t, J = 7.6 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 160.9, 142.9, 142.4, 113.7, 108.6, 107.0, 23.6, 18.2, 15.0, 14.5. HRMS (ESI) calcd for $C_{11}H_{13}NO_2$ $[M + H]^+$ 192.1019, found 192.1017.

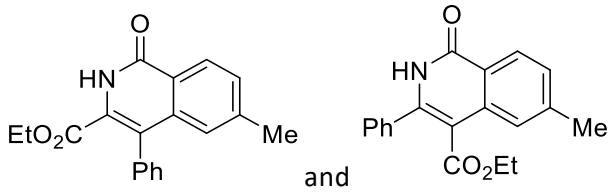
(Furan-3-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide (0.2 mmol, 44 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg), 48 h; 30% yield (11 mg).



Ethyl 4-butyl-6-methyl-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (39) and ethyl 3-butyl-6-methyl-1-oxo-1,2-dihydroisoquinoline-4-carboxylate (40). Ylide **2** (0.2 mmol, 48 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and ethyl hept-2-ynoate (0.4 mmol, 62 mg), 24 h; **Product 39:** white solid; mp 141−142 °C (CH_2Cl_2); 50% yield (29 mg); purification (gradient elution, hexanes/EtOAc, 20% → 40%); R_f = 0.42 (hexanes/EtOAc = 1/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.40 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.46 (d, J = 8.0 Hz, 1H), 4.45 (q, J = 6.9 Hz, 2H), 3.19 (d, J = 7.5 Hz, 2H), 2.56 (s, 3H), 1.66 – 1.57 (m, 2H), 1.57 – 1.49 (m, 2H), 1.45 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 161.0, 143.6, 137.3, 130.6, 128.2, 126.2, 125.5, 125.1, 124.3, 62.6, 32.8, 26.6, 23.3, 22.4, 14.4, 14.1. HRMS (ESI) calcd for $C_{17}H_{21}NO_3$ $[M + H]^+$ 288.1594, found 288.1596.

Product 40: White solid; mp 209−210 °C (CH_2Cl_2); 7% yield (4 mg); R_f = 0.55 (hexanes/EtOAc = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.33 (s, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.62 (s, 1H), 7.30 (d, J = 8.1 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 2.85 – 2.71 (m, 2H), 2.49 (s, 3H), 1.82 – 1.69 (m, 2H), 1.52 – 1.37 (m, 5H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 164.1, 144.6, 144.0, 135.9, 128.2, 127.4, 124.2, 122.0, 109.2, 61.4, 32.5, 31.6, 22.8, 22.4, 14.5, 13.9. HRMS (ESI) calcd for $C_{17}H_{21}NO_3$ $[M + H]^+$ 288.1594, found 288.1596.

Ylide **3** (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL) and ethyl hept-2-ynoate (0.4 mmol, 62 mg), 48 h; **39**: 47% yield (27 mg) and **40**: 7% yield (4 mg).

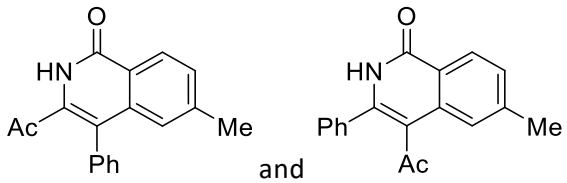


Ethyl 6-methyl-1-oxo-4-phenyl-1,2-dihydroisoquinoline-3-carboxylate (41) and ethyl 6-methyl-1-oxo-3-phenyl-1,2-dihydroisoquinoline-4-carboxylate (42). Ylide **2** (0.2 mmol, 48 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03

mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and ethyl 3-phenylpropiolate (0.4 mmol, 70 mg). 24 h; **Product 41:** white solid; mp 181−182 °C (CH_2Cl_2); 38% yield (23 mg); purification (gradient elution, hexanes/EtOAc, 20% → 50%); R_f = 0.35 (hexanes/acetone = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.41 (d, J = 8.1 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.29 – 7.19 (m, 2H), 6.97 (s, 1H), 4.07 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 161.3, 143.6, 138.2, 135.9, 130.7, 130.0, 128.3, 127.8, 127.7, 125.6, 125.0, 124.9, 62.2, 22.1, 13.4. One carbon signal could not be located. HRMS (ESI) calcd for $C_{19}H_{17}NO_3$ $[M + H]^+$ 308.1281, found 308.1283. Structure of this compound was verified by X-ray crystallographic analysis after recrystallization from diethyl ether.

Product 42: White solid; mp 197−198 °C (CH_2Cl_2); 18% yield (11 mg); R_f = 0.30 (hexanes/acetone = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.28 (d, J = 8.2 Hz, 1H), 7.71 (s, 1H), 7.50 (q, J = 3.5, 2.4 Hz, 5H), 7.35 (d, J = 8.2 Hz, 1H), 4.07 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 162.7, 144.4, 141.8, 135.4, 135.0, 130.0, 129.0, 128.1, 127.8, 124.4, 122.5, 110.2, 61.3, 22.3, 13.6. One carbon signal could not be located. HRMS (ESI) calcd for $C_{19}H_{17}NO_3$ [M + H]+ 308.1281, found 308.1284.

Ylide **3** (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.04 mmol, 32 mg), pivalic acid (0.06 mmol, 6 mg), HFIP (1 mL), and ethyl hept-2-ynoate (0.4 mmol, 62 mg), 48 h; **41**: 39% yield (24 mg) and **42**: 18% yield (11 mg).

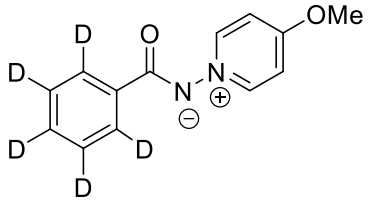


3-Acetyl-6-methyl-4-phenylisoquinolin-1(2H)-one (43) and 4-acetyl-6-methyl-3-phenylisoquinolin-1(2H)-one (44). Ylide **2** (0.2 mmol, 48 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 4-phenylbut-3-yn-2-one (0.4 mmol, 58 mg). 24 h; **Product 43**: white solid; mp 254−255 °C (CH_2Cl_2); 24% yield (13 mg); purification (gradient elution, hexanes/EtOAc, 20% → 60%); R_f = 0.14 (hexanes/EtOAc = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.29 (d, J = 8.1 Hz, 1H), 7.65 – 7.49 (m, 6H), 7.36 (d, J = 8.1 Hz, 1H), 2.49 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 162.9, 144.5, 139.4, 134.9, 134.1, 130.8, 129.5, 129.0, 128.9, 127.9, 124.1, 122.7, 118.6, 32.9, 22.3. HRMS (ESI) calcd for $C_{18}H_{15}NO_2$ $[M + H]^+$ 278.1176, found 278.1176.

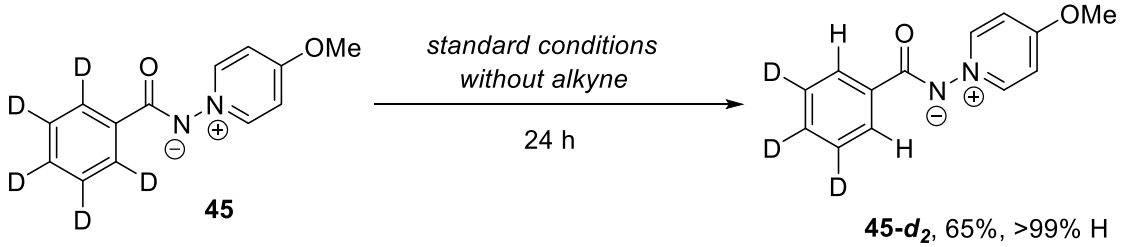
Product 44: White solid; mp 191−192 °C (CH_2Cl_2); 28% yield (16 mg); R_f = 0.23 (hexanes/EtOAc = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.41 (d, J = 8.1 Hz, 1H), 7.65 – 7.52 (m, 3H), 7.45 (d, J = 8.1 Hz, 1H), 7.40 – 7.30 (m, 2H), 6.93 (s, 1H), 2.37 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 161.0, 143.6, 138.2, 135.6, 131.7, 131.1, 130.8, 129.4, 129.2, 128.0, 127.8, 126.0, 125.2, 29.9, 22.1. HRMS (ESI) calcd for $C_{18}H_{15}NO_2$ [M + H]+ 278.1180, found 278.1176.

Ylide **3** (0.2 mmol, 54 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and ethyl hept-2-ynoate (0.4 mmol, 62 mg), 48 h; **43**: 25% yield (14 mg) and **44**: 20% yield (11 mg).

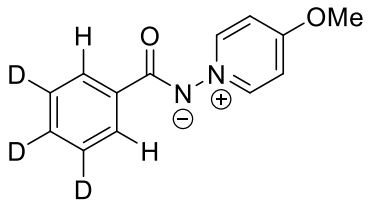
H/D Scrambling experiments



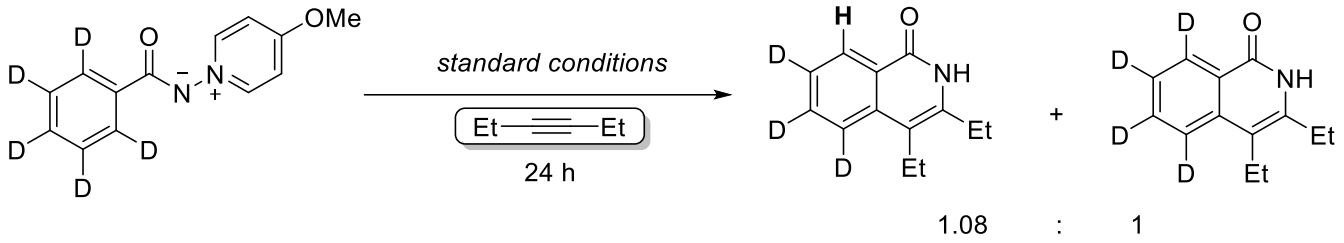
(Benzoyl-2,3,4,5,6-d$_5$)(4-methoxypyridin-1-ium-1-yl)amide (45). Method A was employed, with benzoic-2,3,4,5,6-d_5 acid (0.25 g, 2 mmol). Yield: 0.30 g, 64%; appearance: white solid; ^{1}H NMR (400 MHz, $CDCl_0$) δ 8.52 (d, J = 4.4 Hz, 2H), 7.05 (d, J = 4.4 Hz, 2H), 3.97 (s, 3H).



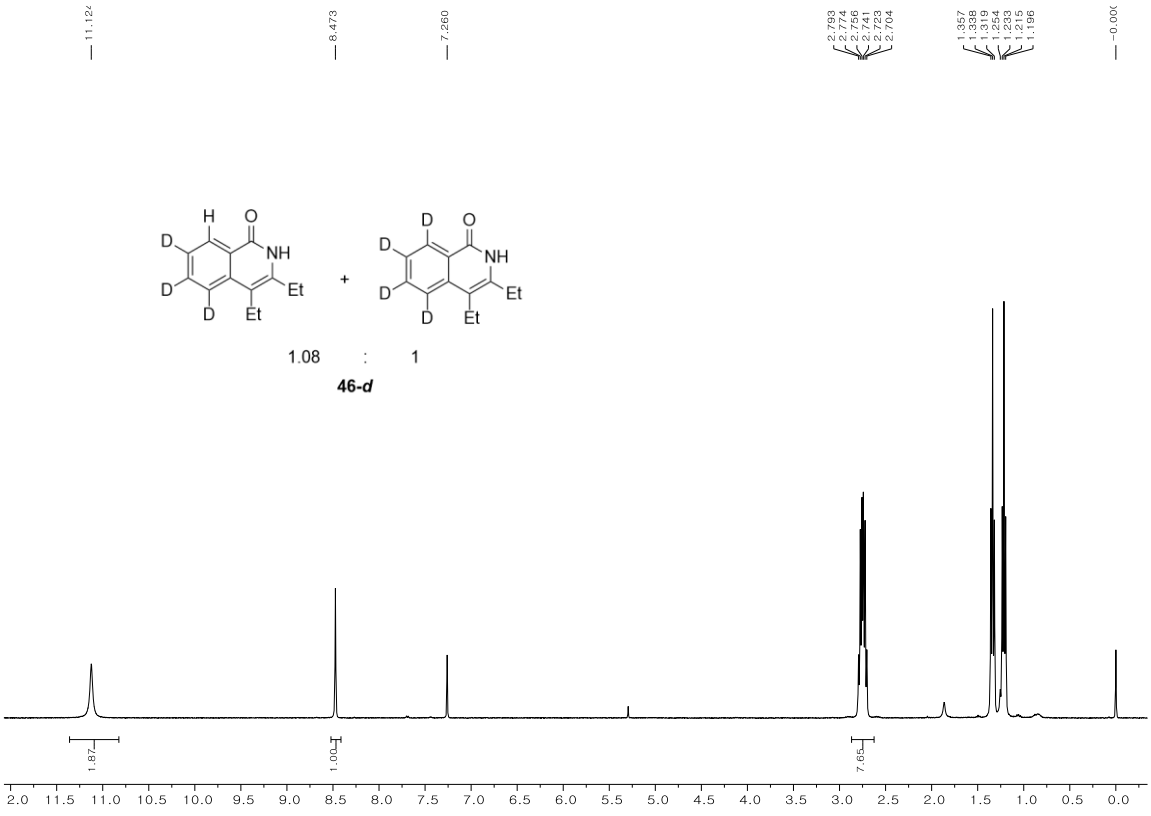
A 2-dram vial equipped with a magnetic stir bar was charged with (benzoyl-2,3,4,5,6-d_5)(4-methoxypyridin-1-ium-1-yl)amide **45** (0.2 mmol, 46 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL). The vial was closed with a screw cap after flushing with nitrogen. The mixture was stirred in a heating block at 110 °C for 24 h. After the mixture was cooled, ethyl acetate was added, and the diluted mixture was poured into a round bottom flask. The mixture was absorbed on 3 g of silica gel and purified by column chromatography on silica gel.

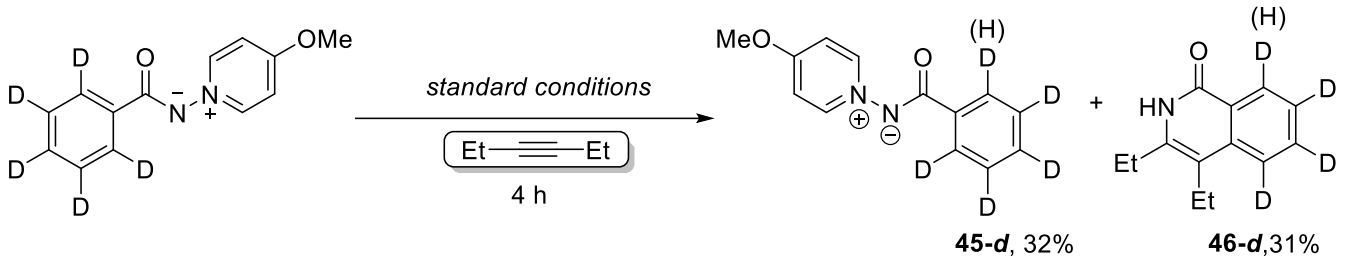


(Benzoyl-3,4,5-d$_3$)(4-methoxypyridin-1-ium-1-yl)amide (45-*d*$_2$). Yield: 30 mg, 65%; Appearance: white solid; purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 6.0 Hz, 2H), 8.13 (s, 2H), 7.07 (d, J = 5.5 Hz, 2H), 3.99 (s, 3H).

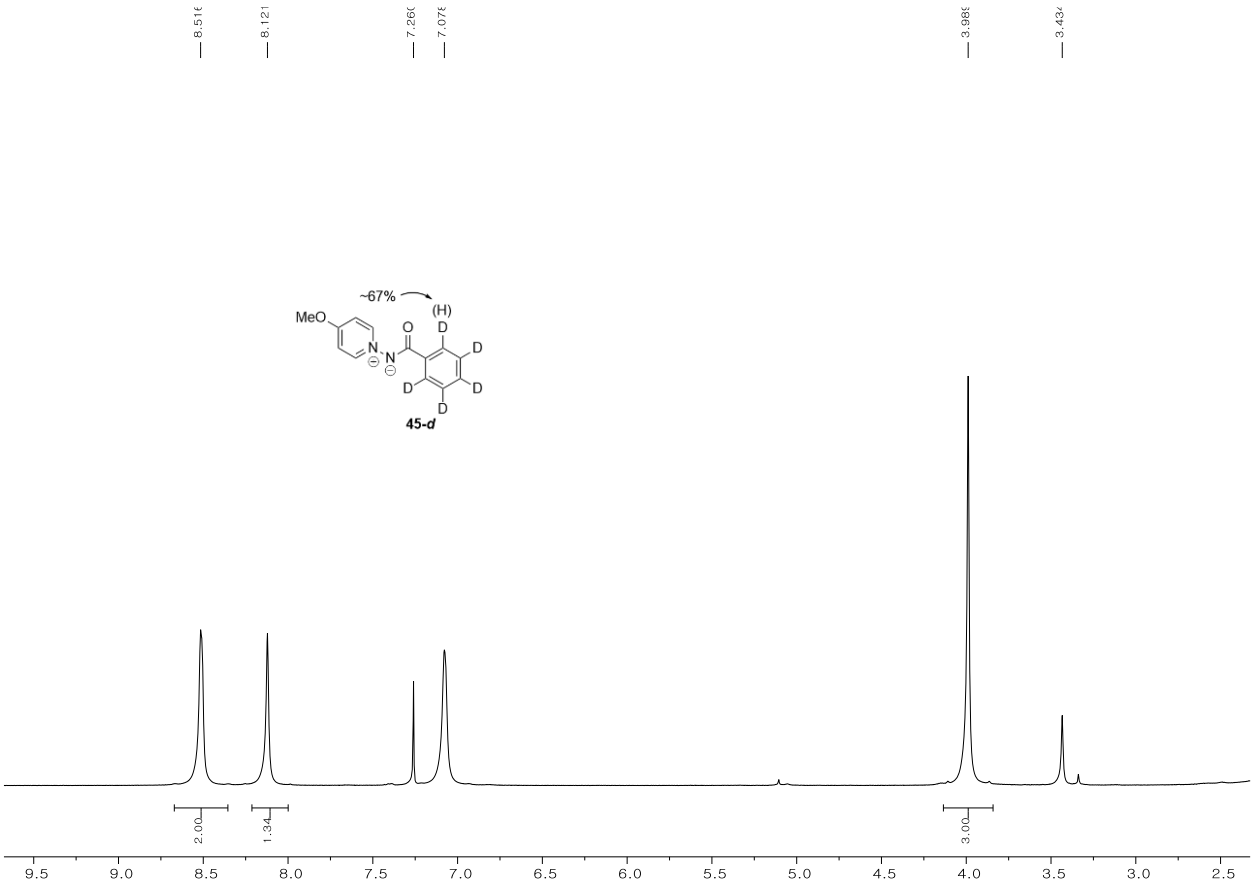


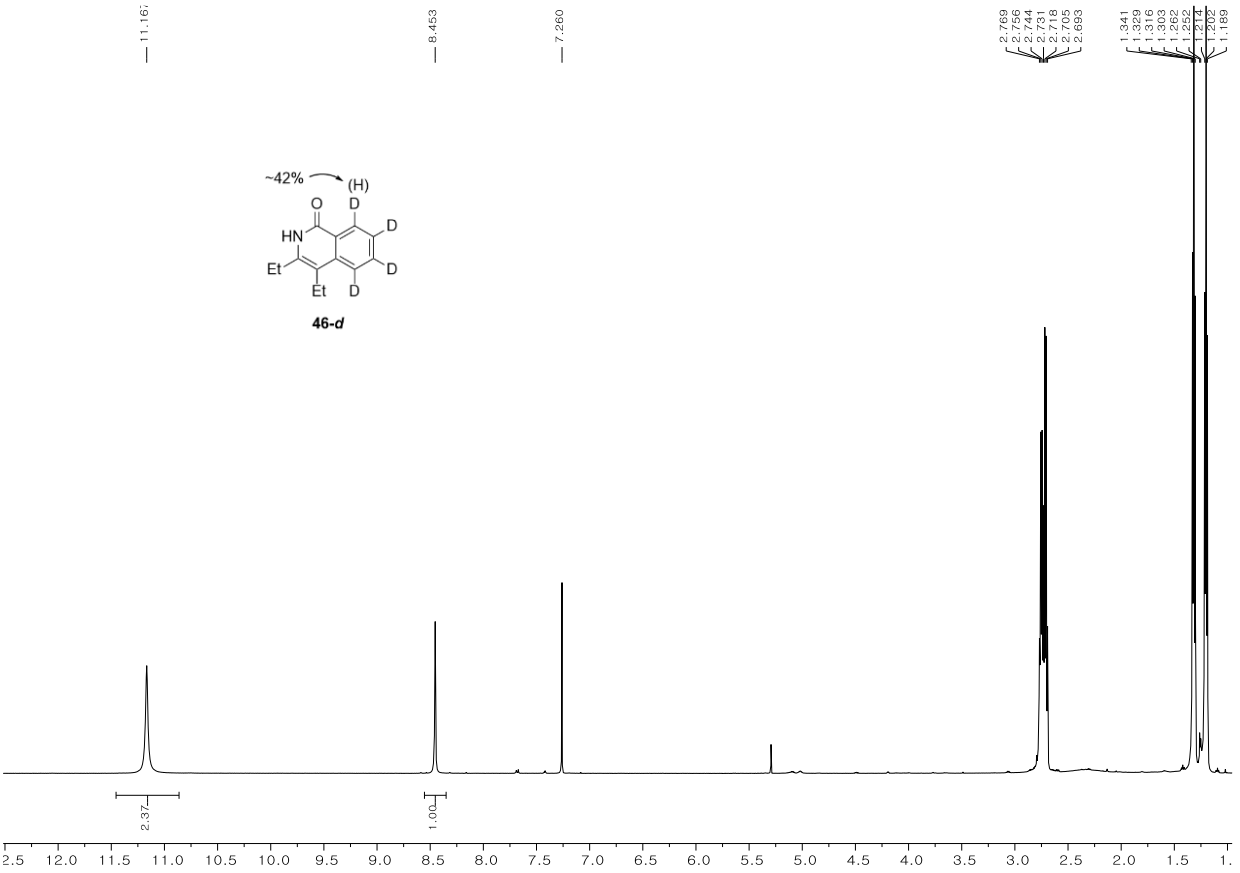
A 2-dram vial equipped with a magnetic stir bar was charged with (benzoyl-2,3,4,5,6-d_5)(4-methoxypyridin-1-ium-1-yl)amide **45** (0.2 mmol, 46 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL). The vial was closed with a screw cap after flushing with nitrogen. The mixture was stirred in a heating block at 110 °C for 24 h. After the mixture was cooled, ethyl acetate was added, and the diluted mixture was poured into a round bottom flask. The mixture was absorbed on 3 g of silica gel and purified by column chromatography on silica gel. The purified mixture was used to check the ratio of products by ^{1}H-NMR spectroscopy.



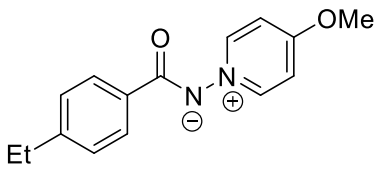


A 2-dram vial equipped with a magnetic stir bar was charged with (benzoyl-2,3,4,5,6-d_5)(4-methoxypyridin-1-ium-1-yl)amide **45** (0.2 mmol, 46 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and 3-hexyne (0.4 mmol, 45 μL). The vial was closed with a screw cap after flushing with nitrogen. The mixture was stirred in a heating block at 110 °C for 4 h. After the mixture was cooled, ethyl acetate was added, and the diluted mixture was poured into a round bottom flask. The mixture was absorbed on 3 g of silica gel and purified by column chromatography on silica gel. The purified mixture was used to check the ratio of products by ^{1}H-NMR spectroscopy.

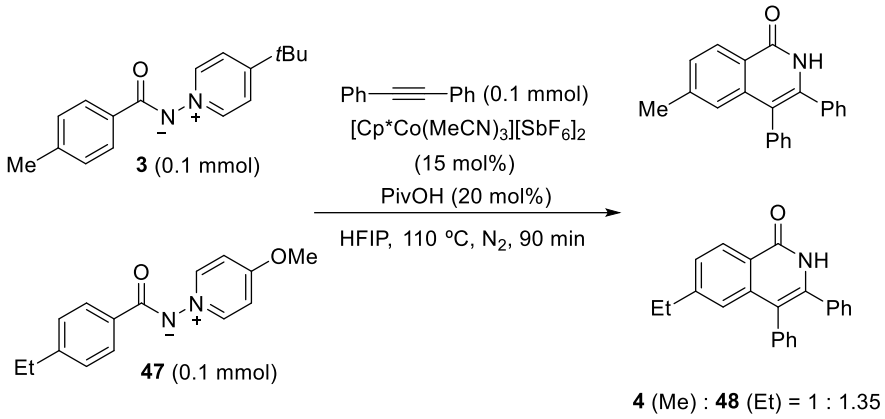




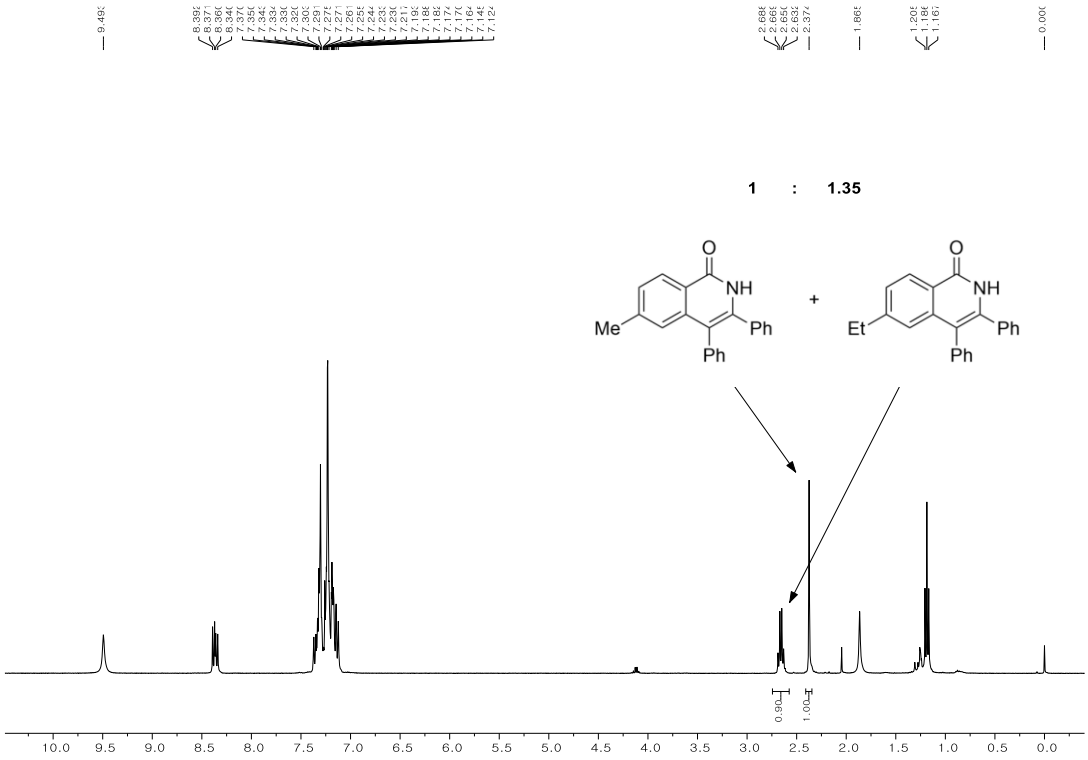
Intermolecular competition experiment between (4-(*tert*-butyl)pyridin-1-ium-1-yl)(4-methylbenzoyl)amide and (4-ethylbenzoyl)(4-methoxypyridin-1-ium-1-yl)amide.



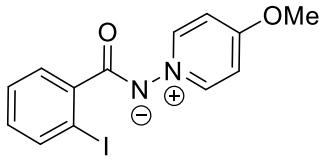
(4-Ethylbenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (47). Method A was employed, with 4-ethylbenzoic acid (0.60 g, 4 mmol). Yield: 0.62 g, 60%; Appearance: white solid; mp 179−180 °C (EtOAc/MeOH = 10:1); R_f = 0.37 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 5.8 Hz, 1H), 8.04 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.05 (d, J = 5.8 Hz, 1H), 3.96 (s, 1H), 2.67 (q, J = 7.1 Hz, 1H), 1.24 (t, J = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 166.0, 146.4, 145.2, 134.8, 128.0, 127.5, 111.4, 56.9, 28.9, 15.6.



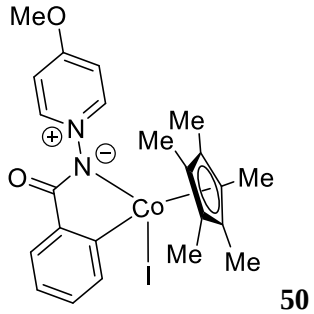
A 2-dram vial equipped with a magnetic stir bar was charged with (4-(*tert*-butyl)pyridin-1-ium-1-yl)(4-methylbenzoyl)amide (0.1 mmol, 27 mg), (4-ethylbenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.1 mmol, 26 mg), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.03 mmol, 24 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.1 mmol, 18 mg). The vial was closed with a screw cap after flushing with nitrogen. The mixture was stirred in a heating block at 110 °C for 90 min. After the mixture was cooled, ethyl acetate was added, and the diluted mixture was poured into a round bottom flask. The mixture was absorbed on 3 g of silica gel and purified by column chromatography on silica gel. The purified mixture was used to check the ratio of products by ^{1}H-NMR spectroscopy.



Preparation of cobaltacycles

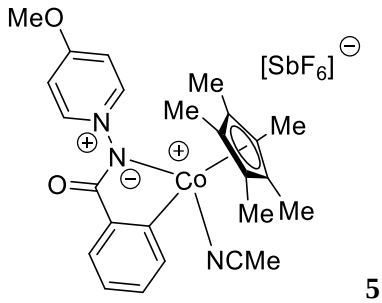


(2-Iodobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (49). Method A was employed, with 2-iodobenzoic acid (0.99 g, 4 mmol). Yield: 0.92 g, 65%; appearance: white solid; mp 195−196 °C (EtOAc/MeOH = 10:1); R_f = 0.37 (EtOAc/MeOH = 5/1); purification (gradient elution, EtOAc/MeOH, 0% → 15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 6.5 Hz, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.15 – 7.05 (m, 2H), 6.99 (t, J = 7.6 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 166.4, 144.7, 144.4, 139.4, 129.6, 128.6, 128.0, 111.7, 94.8, 57.0.



50

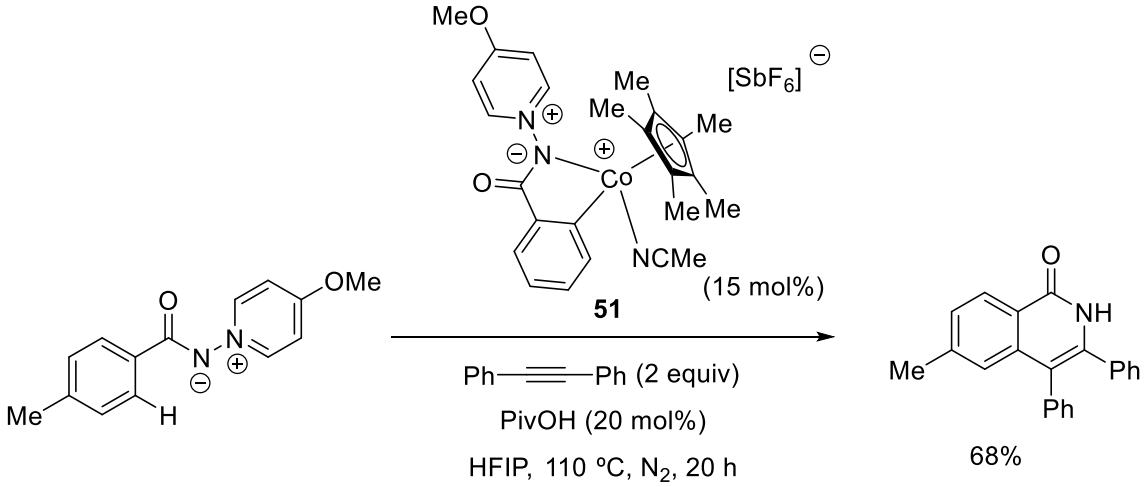
The oven dried flask was charged with $Co_2(CO)_8$ (0.5 mmol, 0.17 g), CH_2Cl_2 (50 mL), and 1,2,3,4,5-pentamethylcyclopentadiene (1.2 mmol, 188 μL). The mixture was refluxed under a nitrogen atmosphere for 4 h and cooled to room temperature. The solvent was removed under vacuum. The residue was dissolved in THF (10 mL). (2-Iodobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (0.95 mmol, 0.34 g) as a solution in THF (30 mL) was added to the solution at room temperature and refluxed for 20 h under a nitrogen atmosphere. After removal of the solvent, the resulting residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc 1:1 to CH_2Cl_2/EtOAc/MeOH 5:5:1) to provide the complex **50** (0.39 g, 74%). Structure of this compound was verified by X-ray crystallographic analysis after recrystallization from CH_2Cl_2 and diethyl ether at room temperature. appearance: black olive solid; R_f = 0.50 (CH_2Cl_2/EtOAc/MeOH = 5/5/1); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 9.34 (s, 2H), 8.36 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.1 Hz, 2H), 7.25 – 7.10 (m, 2H), 7.03 (t, J = 7.3 Hz, 1H), 3.98 (s, 3H), 1.33 (s, 15H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 177.3, 173.7, 168.3, 148.2, 142.7, 139.4, 130.6, 126.3, 122.5, 112.0, 91.8, 58.1, 10.4. HRMS (ESI) calcd for $C_{23}H_{26}CoIN_2O_2$ $[M - I]^+$ 421.1321, found 421.1330.



51

To a flask was added pyidinium ylide cobaltacycle **50** (0.11 g, 0.2 mmol) and CH_3CN (3 mL). To the solution was added the solution of $AgSbF_6$ (0.08 g, 0.24 mmol) in CH_3CN (5 mL) dropwise at room temperature. The suspension was stirred for 2 h at room temperature under a nitrogen atmosphere. Then the suspension was filtered through celite and washed with CH_3CN (5 mL). After removal of the solvent, the resulting solid **51** was used without further purification. Yield: 120 mg, 86%; appearance: dark purple solid; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.63 (d, J = 6.7 Hz, 2H), 8.17 (d, J = 7.7 Hz, 1H), 7.63 – 7.41 (m, 4H), 7.23 – 7.07 (m, 1H), 4.13 (s, 3H), 2.25 (s, 3H), 1.24 (s, 15H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 169.6, 169.3, 147.5, 139.7, 138.7, 138.5, 132.1, 127.3, 124.5, 113.2, 95.4, 58.4, 58.4, 9.4, 4.5.

The use of cationic cobaltacycle 51 as a catalyst.

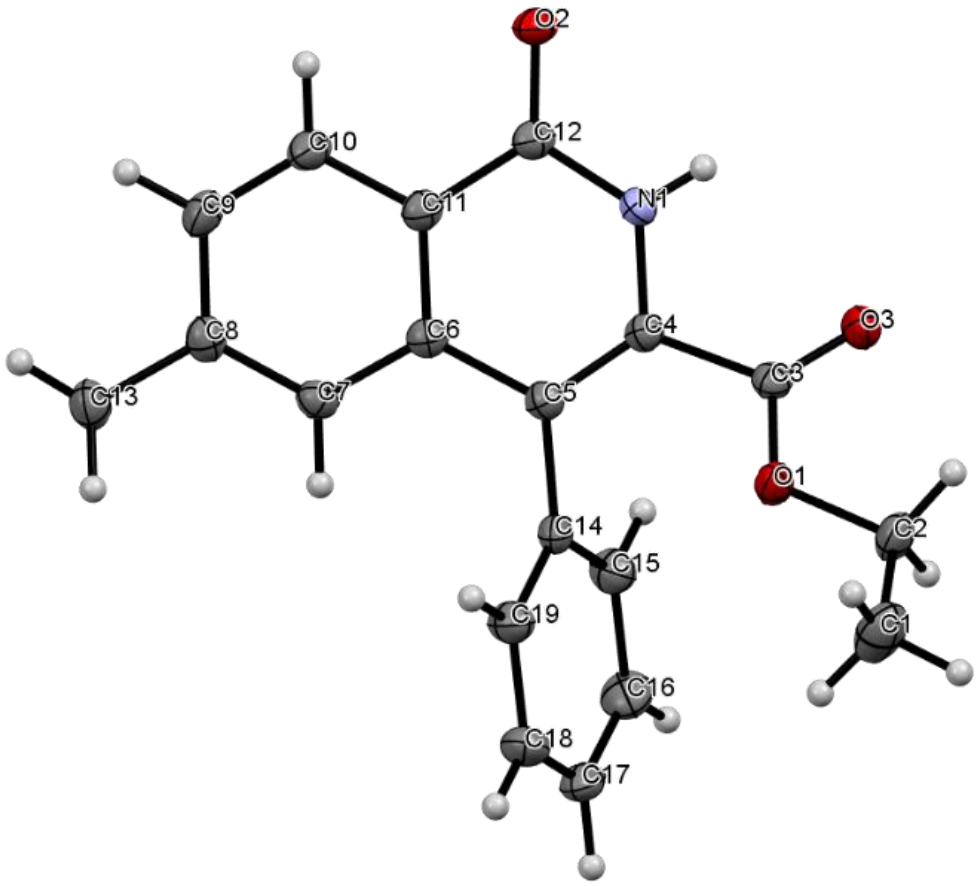


A 2-dram vial equipped with a magnetic stir bar was charged with (4-methoxypyridin-1-ium-1-yl)(4-methylbenzoyl)amide (0.2 mmol, 48 mg), pyridinium ylide cationic cobaltacycle **51** (0.03 mmol, 21 mg), pivalic acid (0.04 mmol, 4 mg), HFIP (1 mL), and diphenylacethylene (0.4 mmol, 71 mg). The vial was closed with a screw cap after flushing with nitrogen. The mixture was stirred in a heating block at 110 °C for 20 h. After the mixture was cooled, ethyl acetate was added, and the diluted mixture was poured into a round bottom flask. The mixture was absorbed on 3 g of silica gel and purified by column chromatography on silica gel. The purified mixture was used to check the yield (68%) using 1,3,5-trimethoxybenzene as an internal standard.

X-Ray Crystallography Data

Table. Crystal data and structure refinement for compound 41.	
Identification code	**Compound 41**
Empirical formula	$C_{19}H_{17}NO_3$
Formula weight	307.33
Temperature/K	123(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.7539(7)
b/Å	15.7753(11)
c/Å	10.6322(7)
α/°	90
β/°	118.742(2)
γ/°	90
Volume/Å^3	1581.48(19)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.709
F(000)	648.0
Crystal size/mm^3	0.37 × 0.32 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.38 to 135.708
Index ranges	$-10 \leq h \leq 12$, $-17 \leq k \leq 18$, $-12 \leq l \leq 12$
Reflections collected	12200
Independent reflections	2801 [R_{int} = 0.0193, R_{sigma} = 0.0208]
Data/restraints/parameters	2801/0/213
Goodness-of-fit on F^2	1.003
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0332, wR_2 = 0.0896
Largest diff. peak/hole / e Å^{-3}	0.21/-0.16

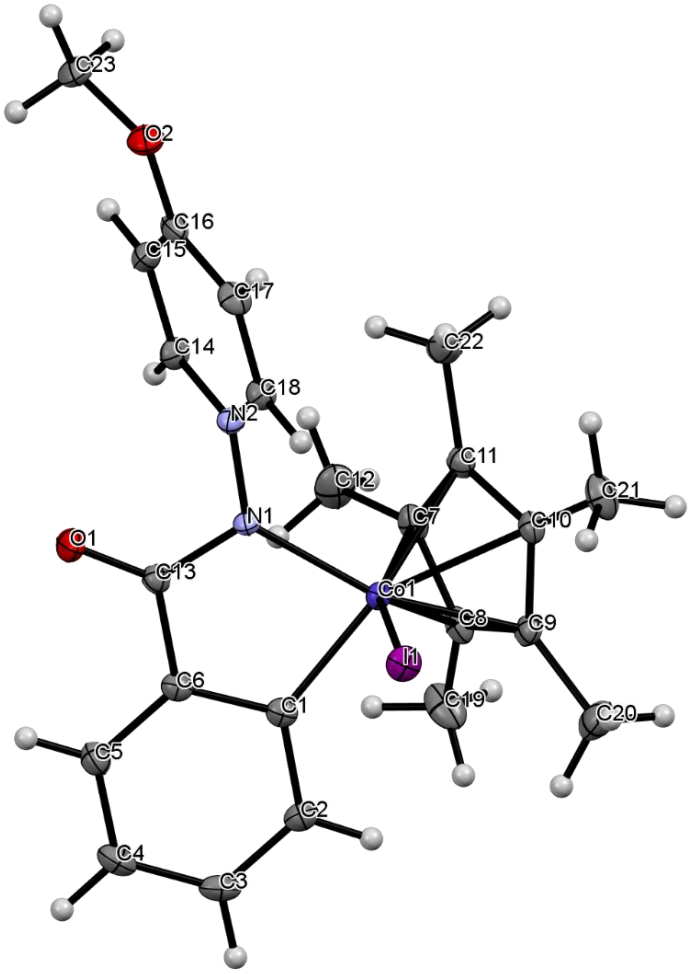
Ethyl 6-methyl-1-oxo-4-phenyl-1,2-dihydroisoquinoline-3-carboxylate (41).



X-Ray Crystallography Data

Table. Crystal data and structure refinement for compound 50.	
Identification code	**50**
Empirical formula	C23 H26 Co I N2 O2
Formula weight	548.29
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 8.4964(11) Å = 90°.
	b = 31.850(4) Å = 112.618(3)°
	c = 8.5016(10) Å = 90°.
Volume	2123.7(4) $Å^3$
Z	4
Density (calculated)	1.715 Mg/m^3
Absorption coefficient	2.284 mm^{-1}
F(000)	1096
Crystal size	0.36 x 0.15 x 0.02 mm^3
Theta range for data collection	2.597 to 28.296°
Index ranges	-11<=h<=11, -42<=k<=42, -11<=l<=11
Reflections collected	20830
Independent reflections	5278 [R(int) = 0.0280]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Empirical
Max. and min. transmission	0.7457 and 0.5814
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5278 / 0 / 268
Goodness-of-fit on F^2	1.227
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0603
R indices (all data)	R1 = 0.0354, wR2 = 0.0614
Largest diff. peak and hole	0.636 and -0.762 e.$Å^{-3}$

50


C23
O2
C16
C15
C17
C14
C18
N2
C22
C11
C12
C21
N1
C7
C10
O1
C13
Co1
C8
C9
I1
C6
C1
C19
C20
C5
C2
C4
C3

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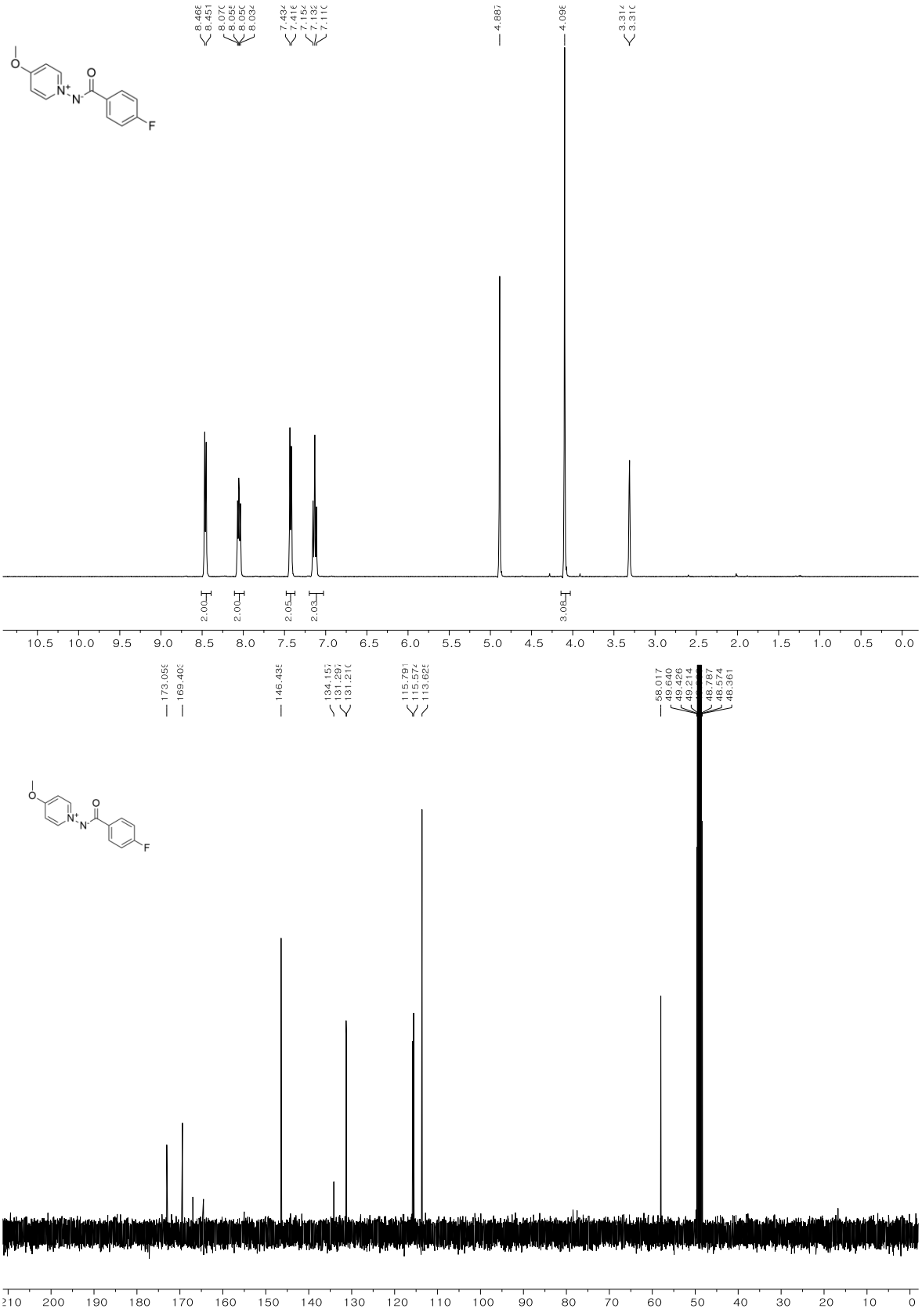
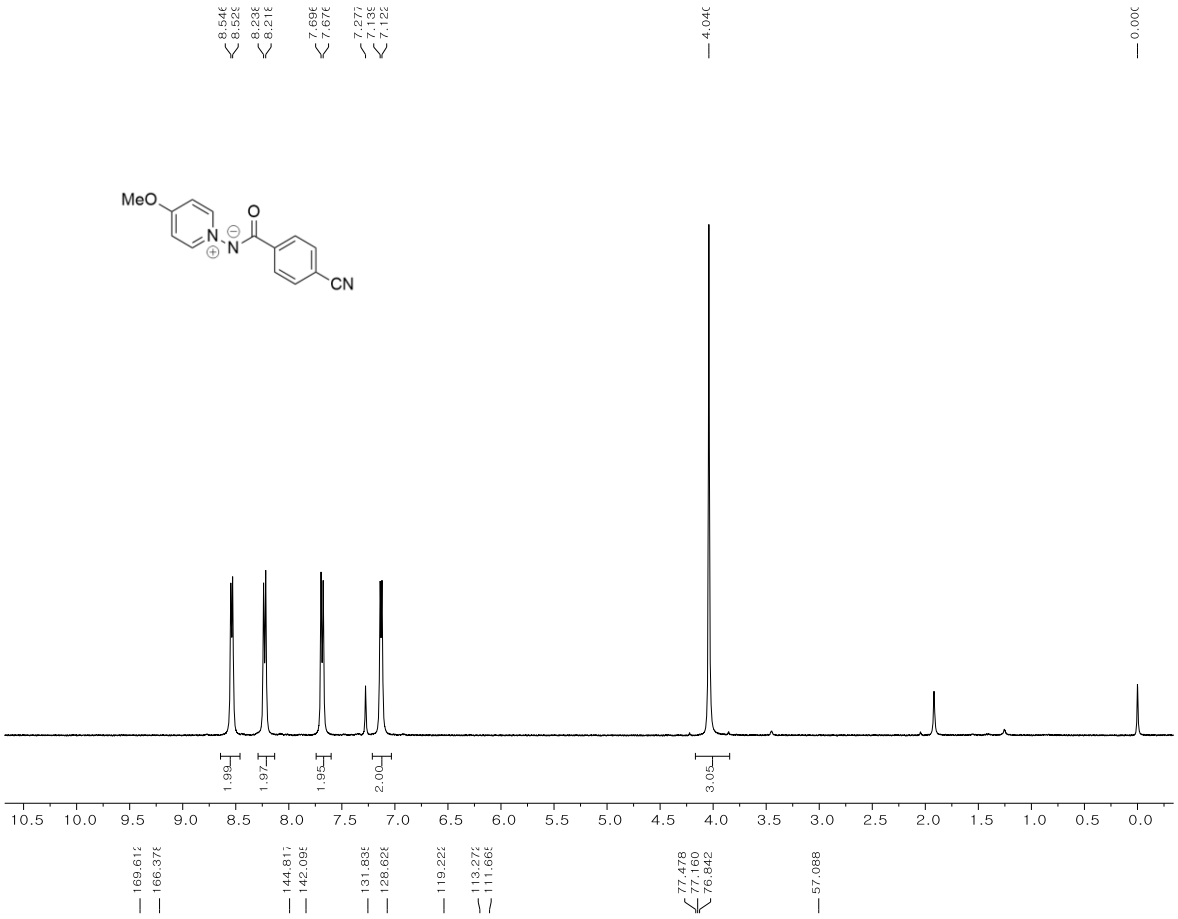
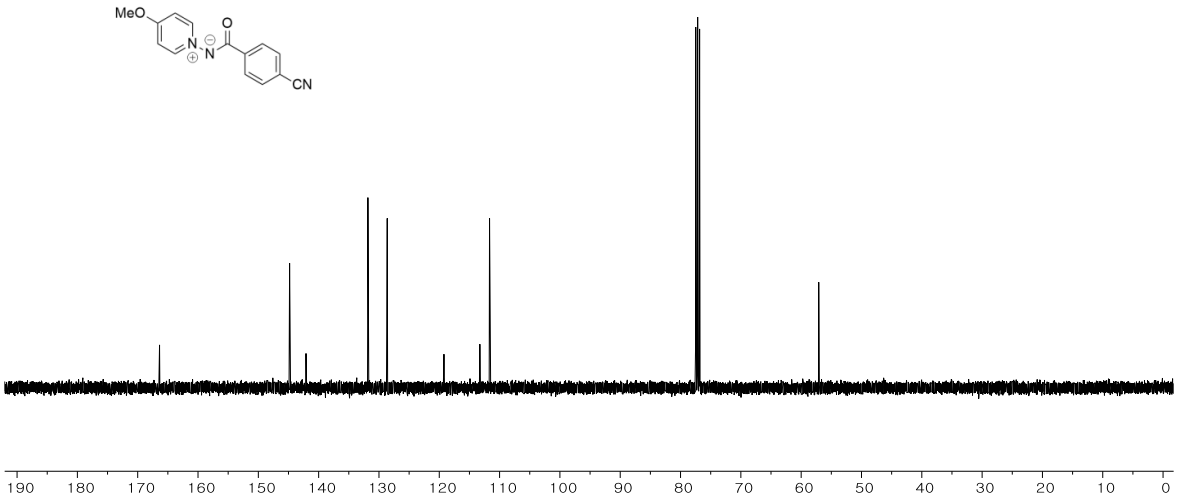
(4-Fluorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

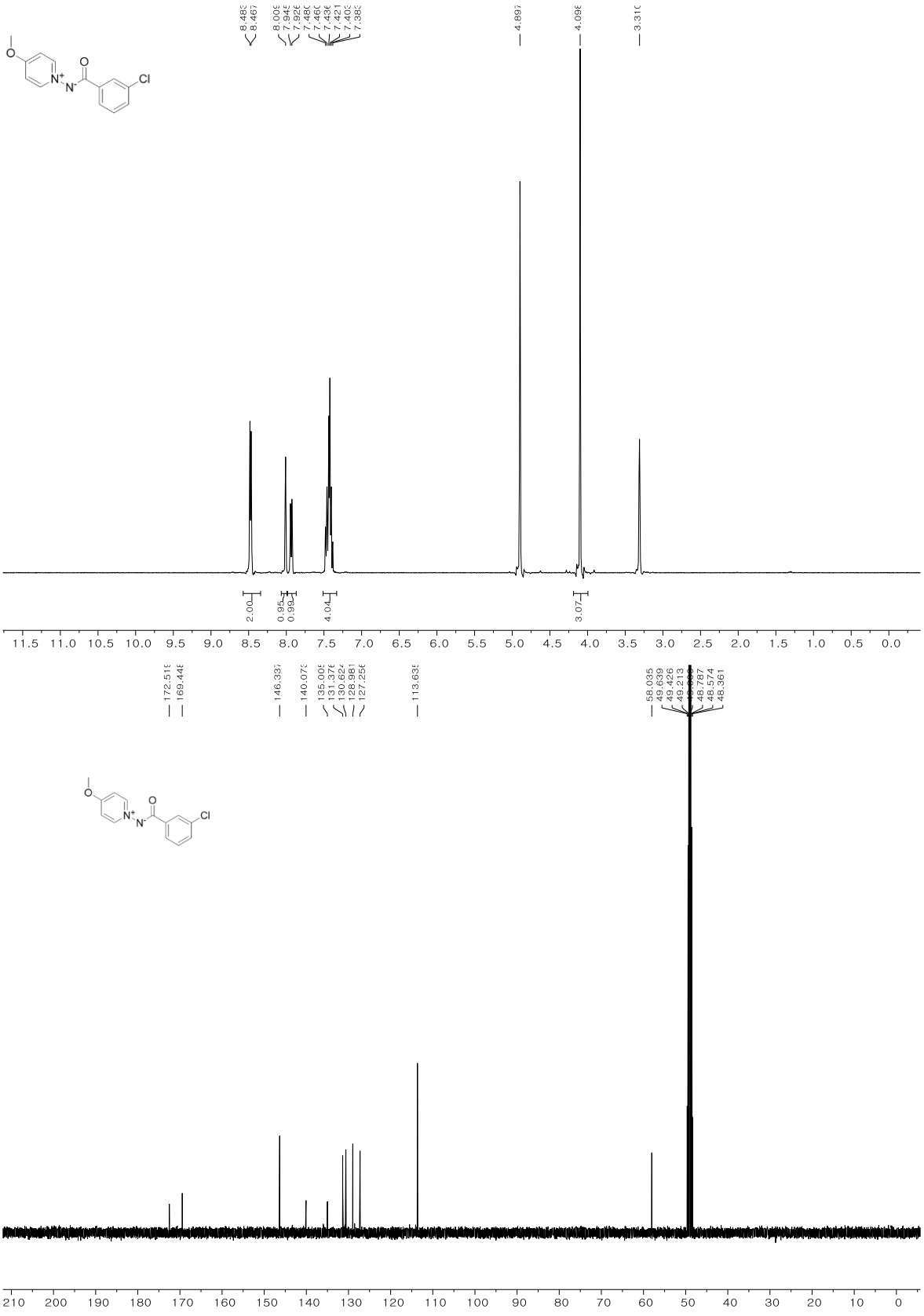


(4-Cyanobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

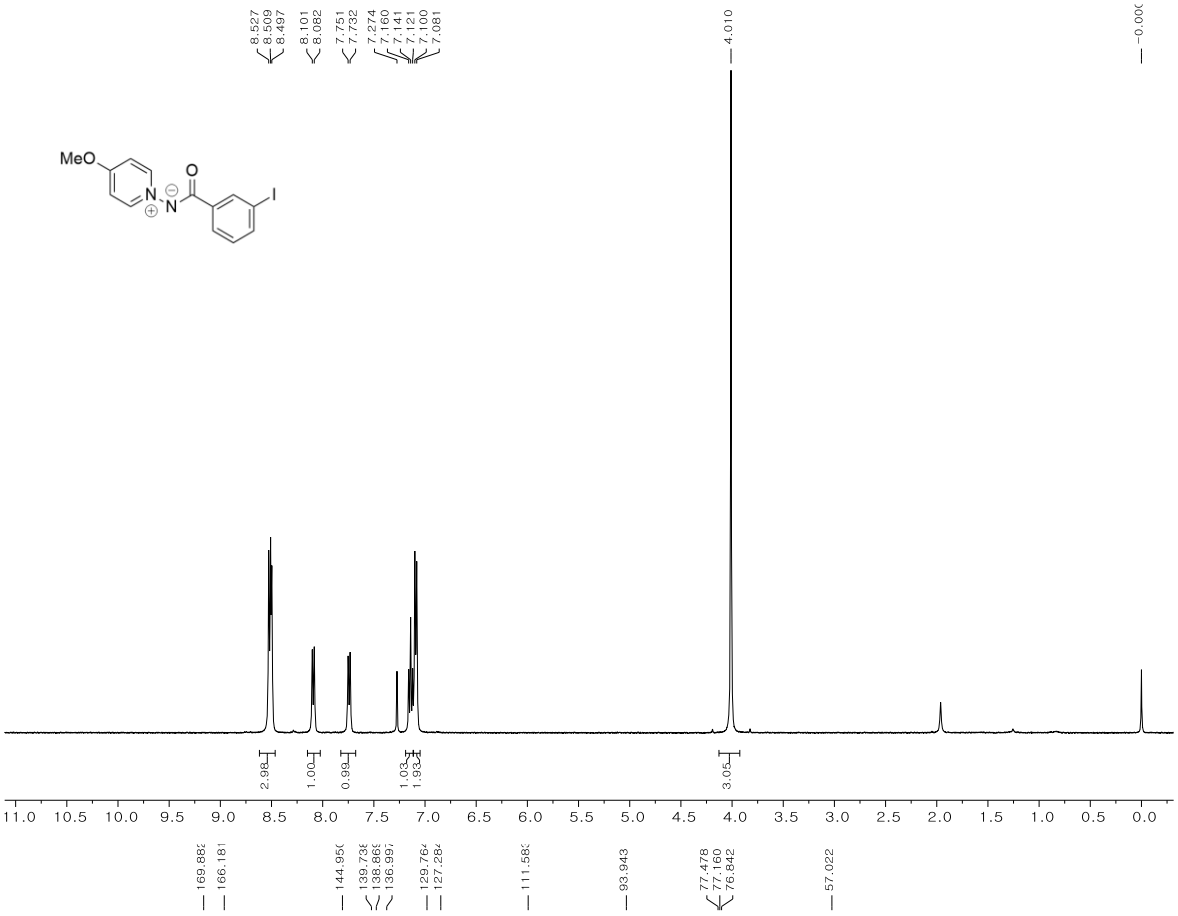




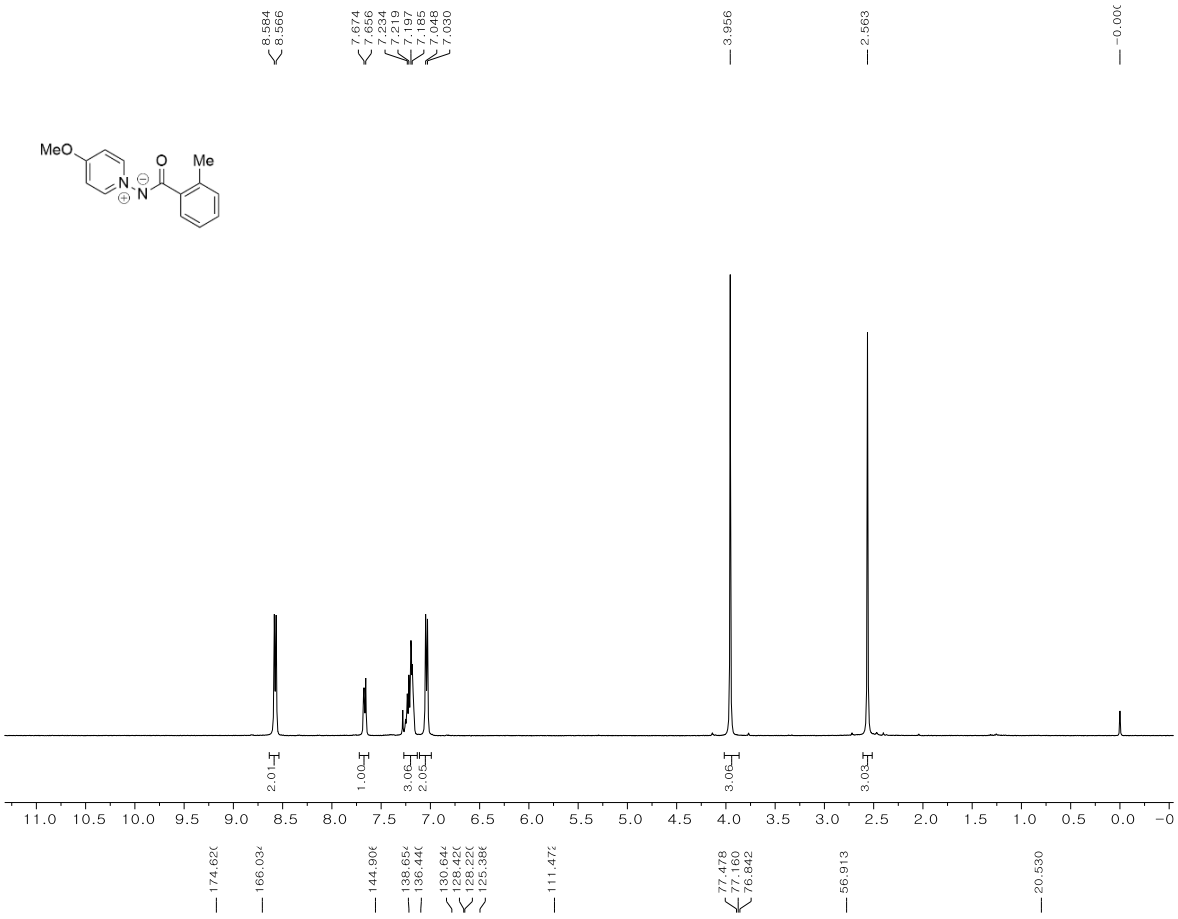
(3-Chlorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

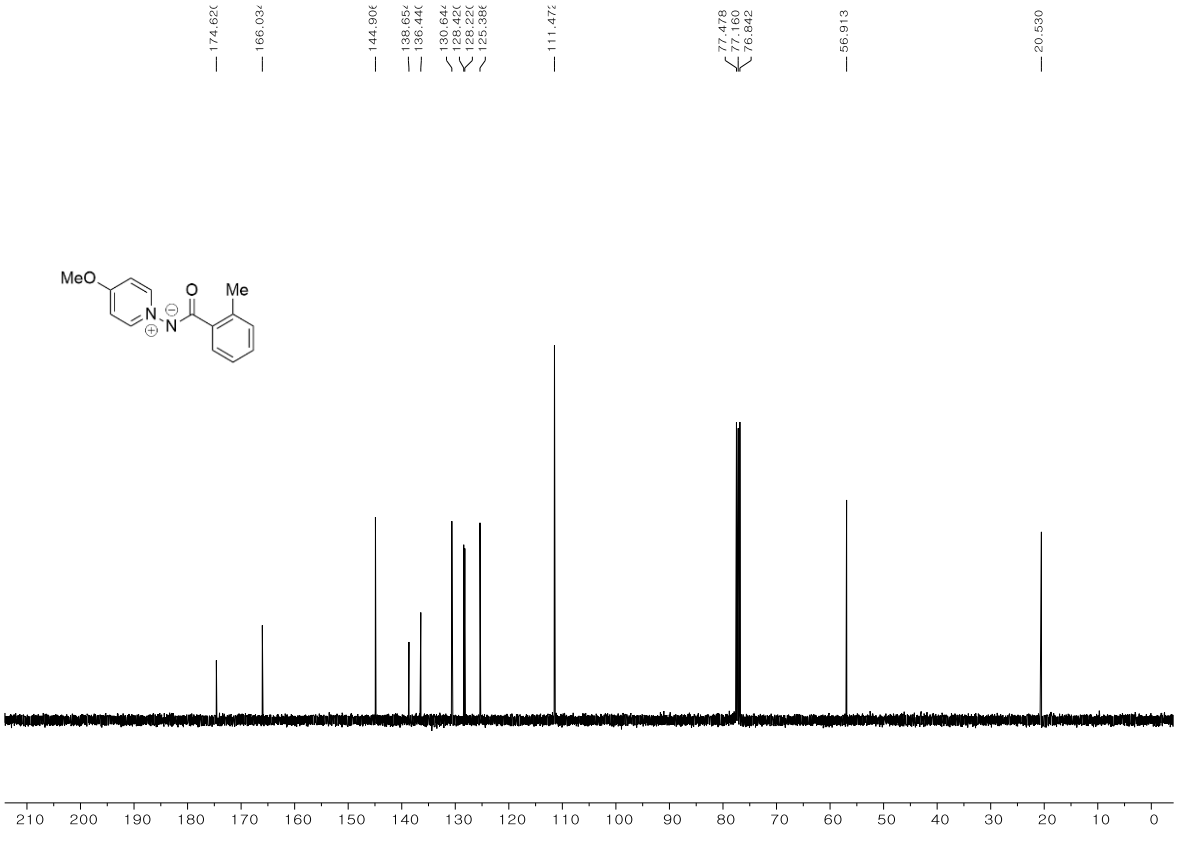


(3-Iodobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

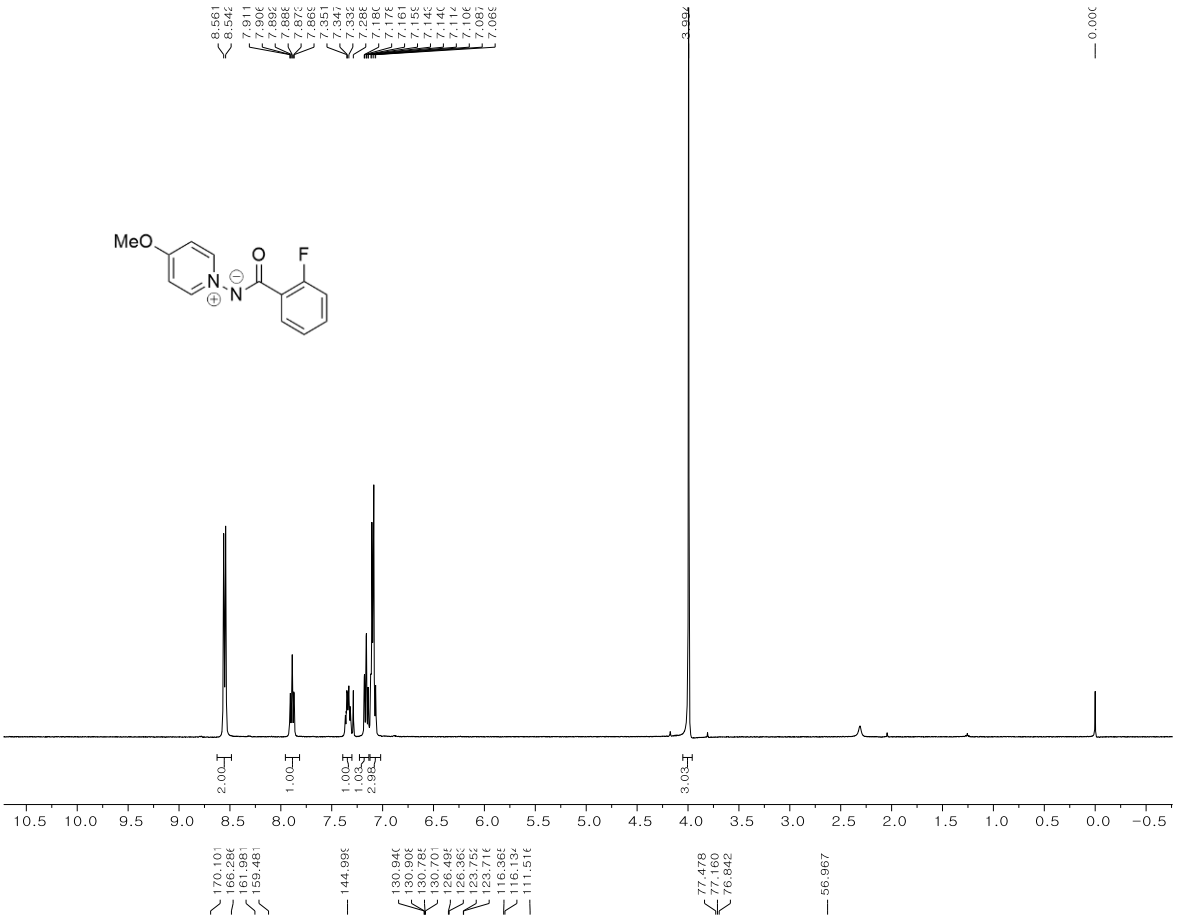


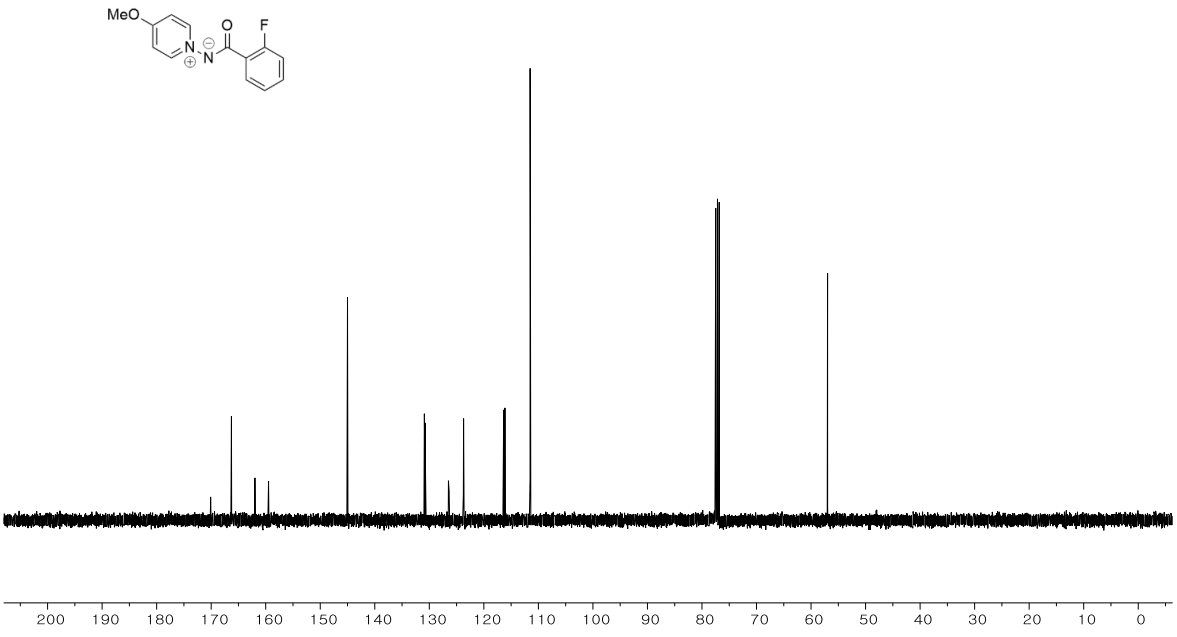
(4-Methoxypyridin-1-ium-1-yl)(2-methylbenzoyl)amide



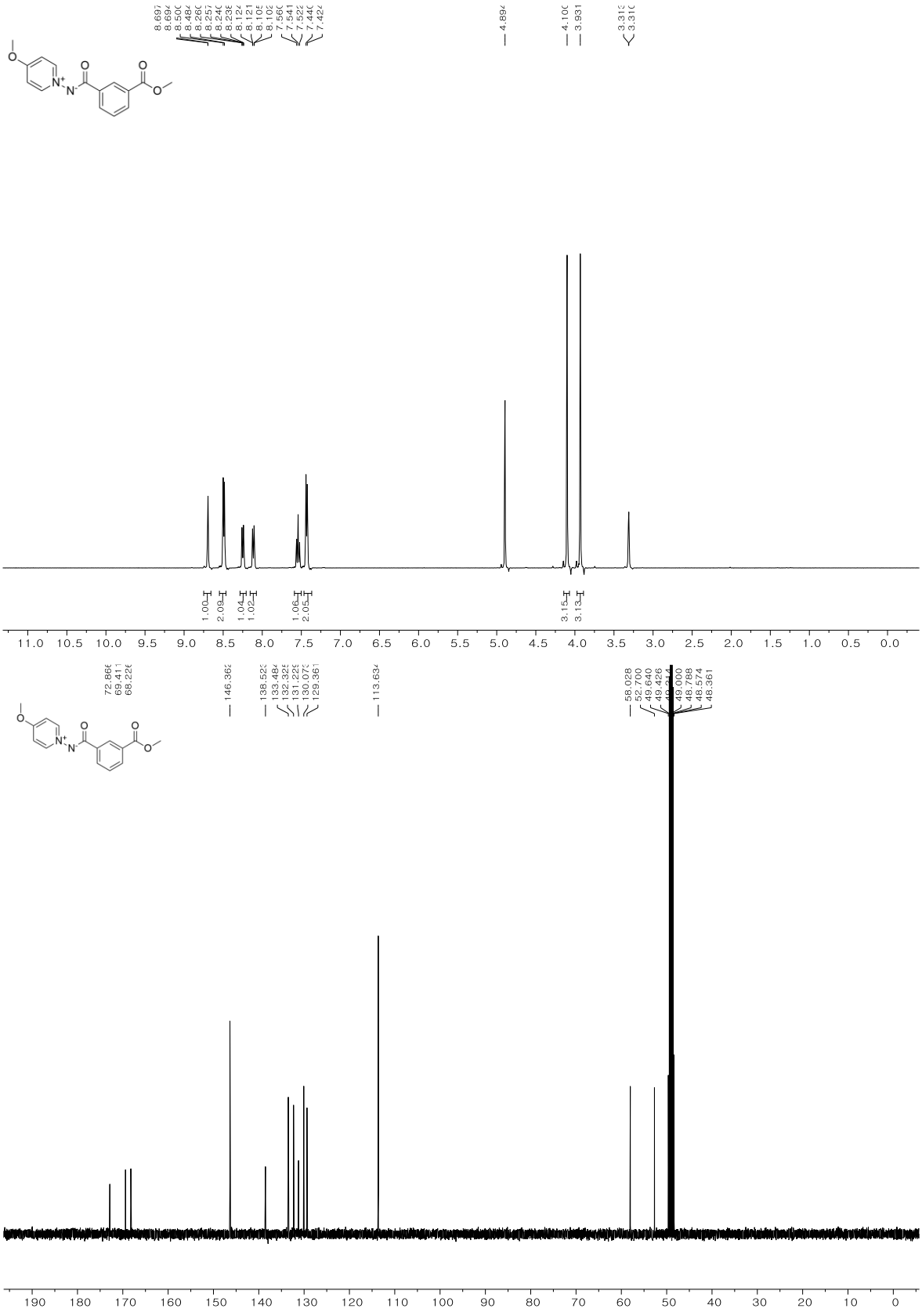


(2-Fluorobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide

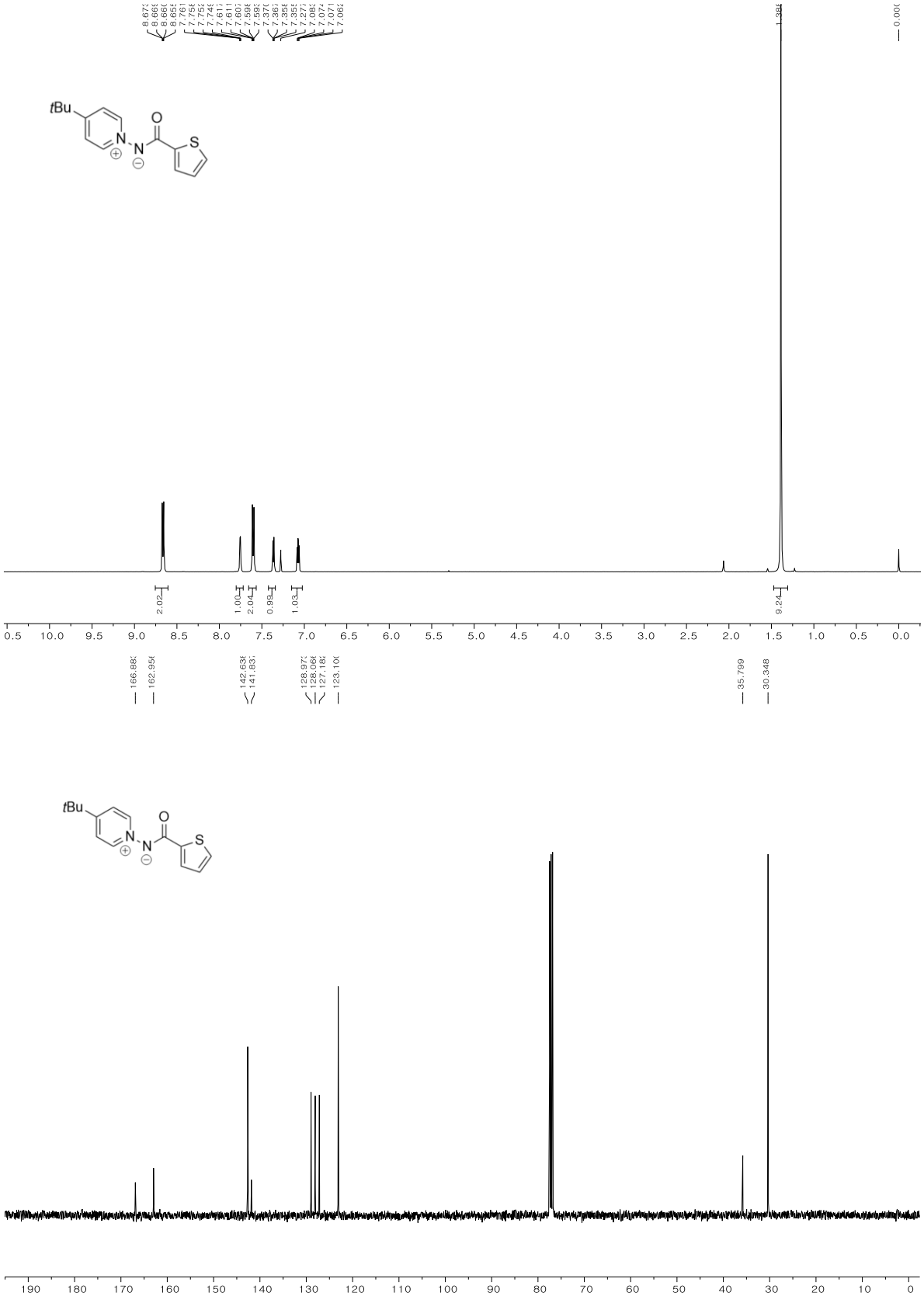




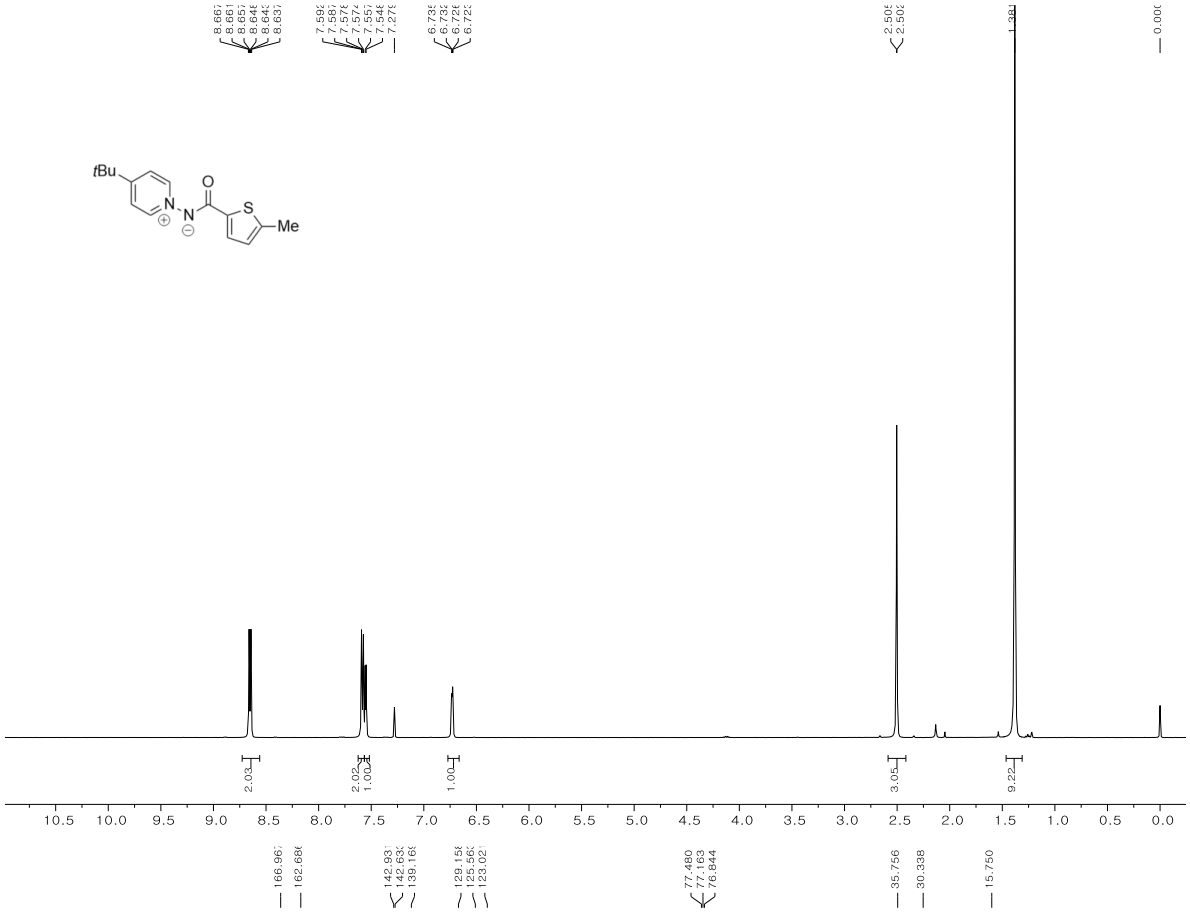
(3-(Methoxycarbonyl)benzoyl)(4-methoxypyridin-1-ium-1-yl)amide

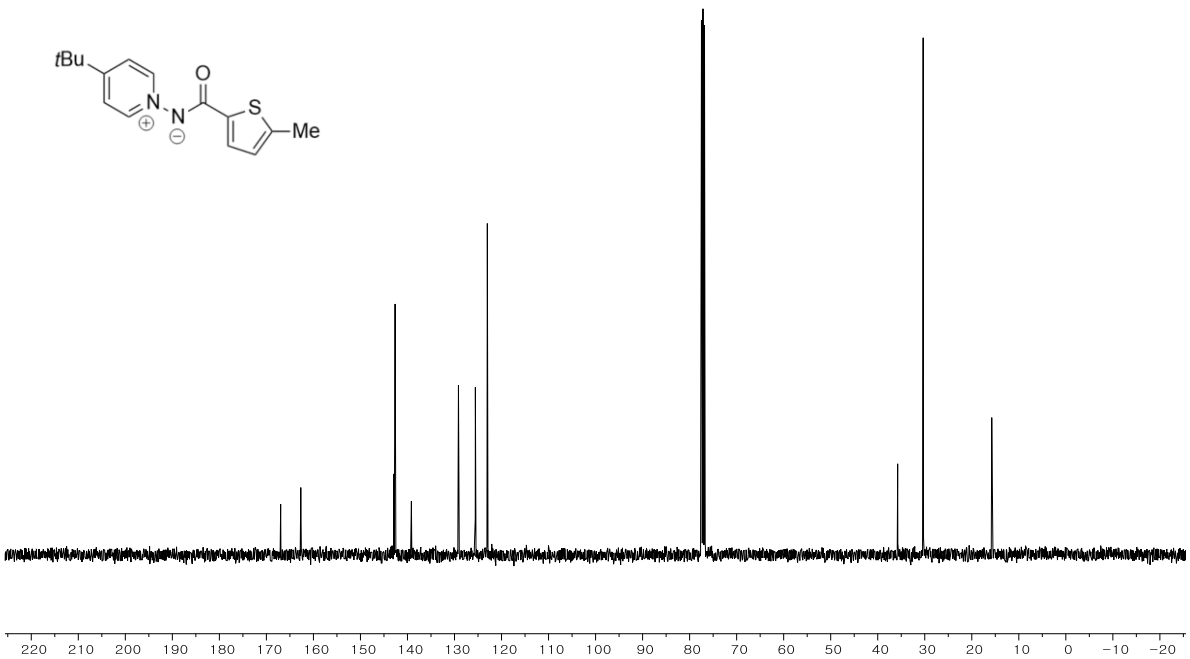


(4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-2-carbonyl)amide

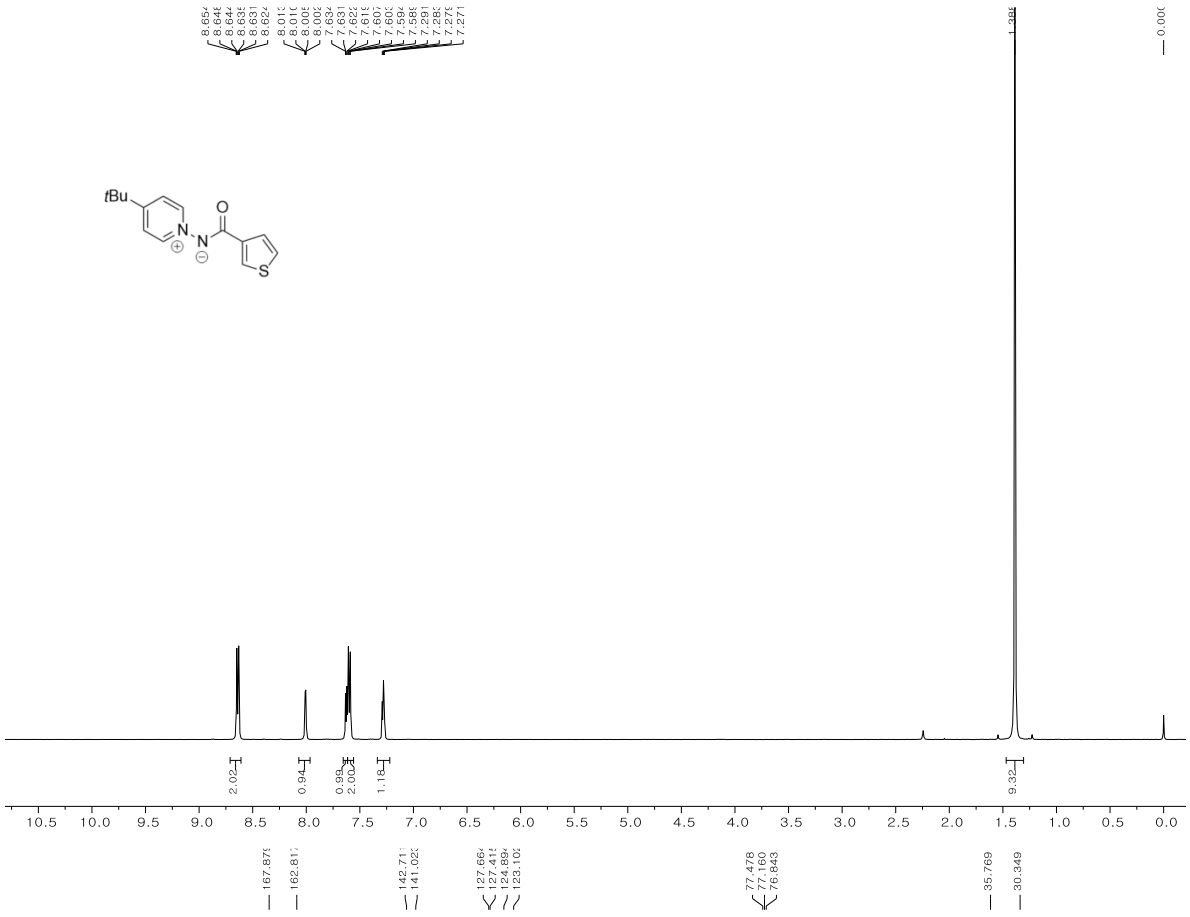


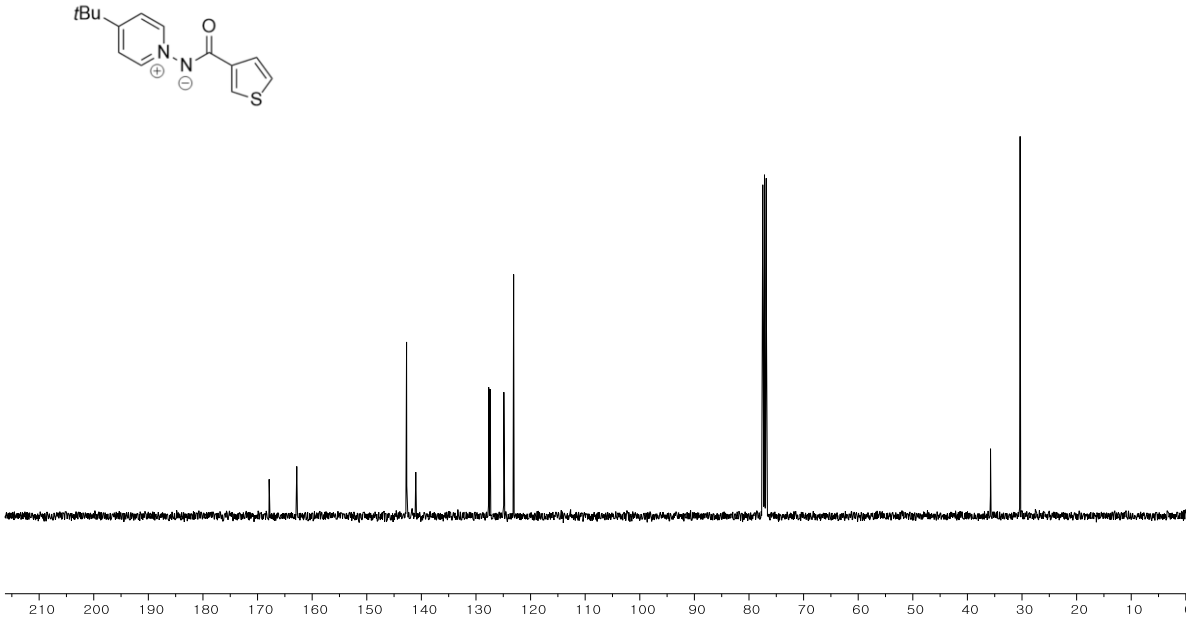
(4-(tert-Butyl)pyridin-1-ium-1-yl)(5-methylthiophene-2-carbonyl)amide



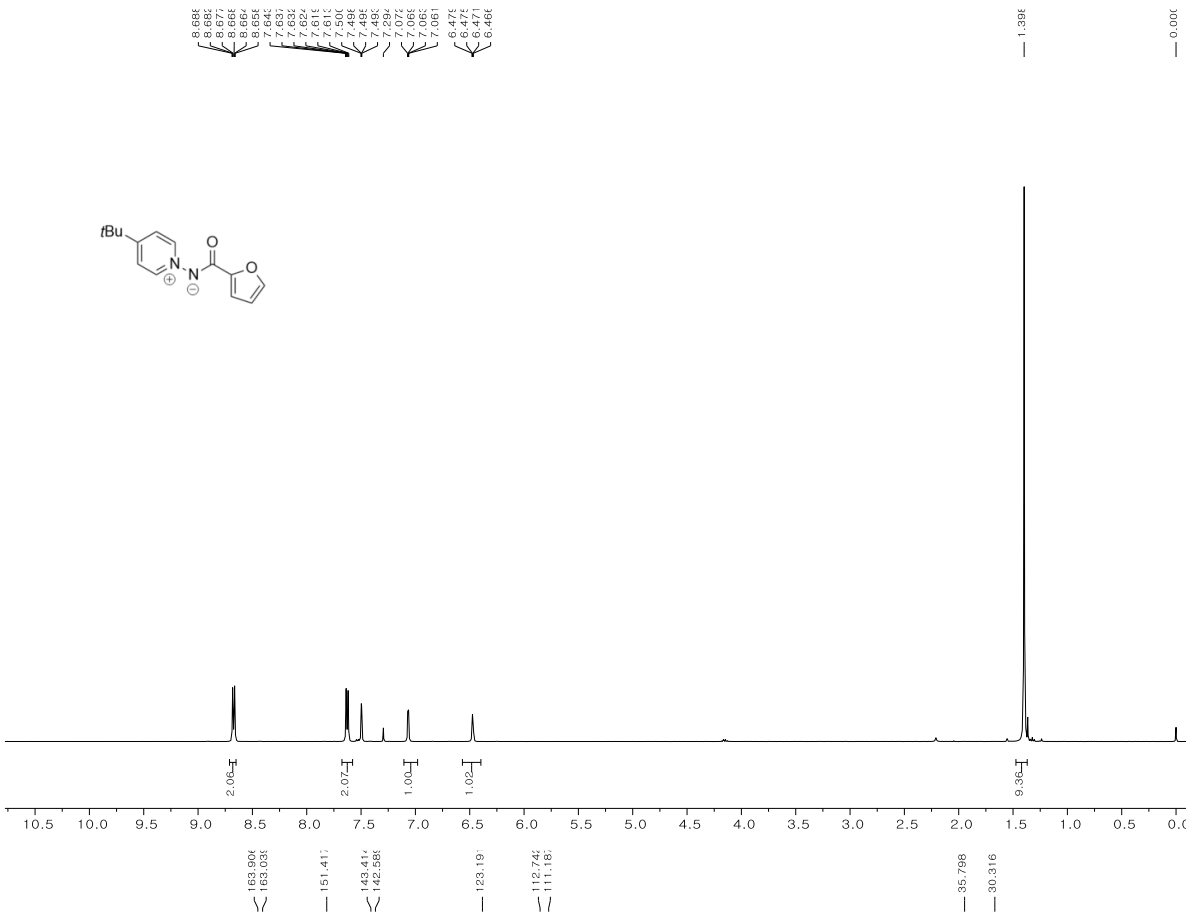


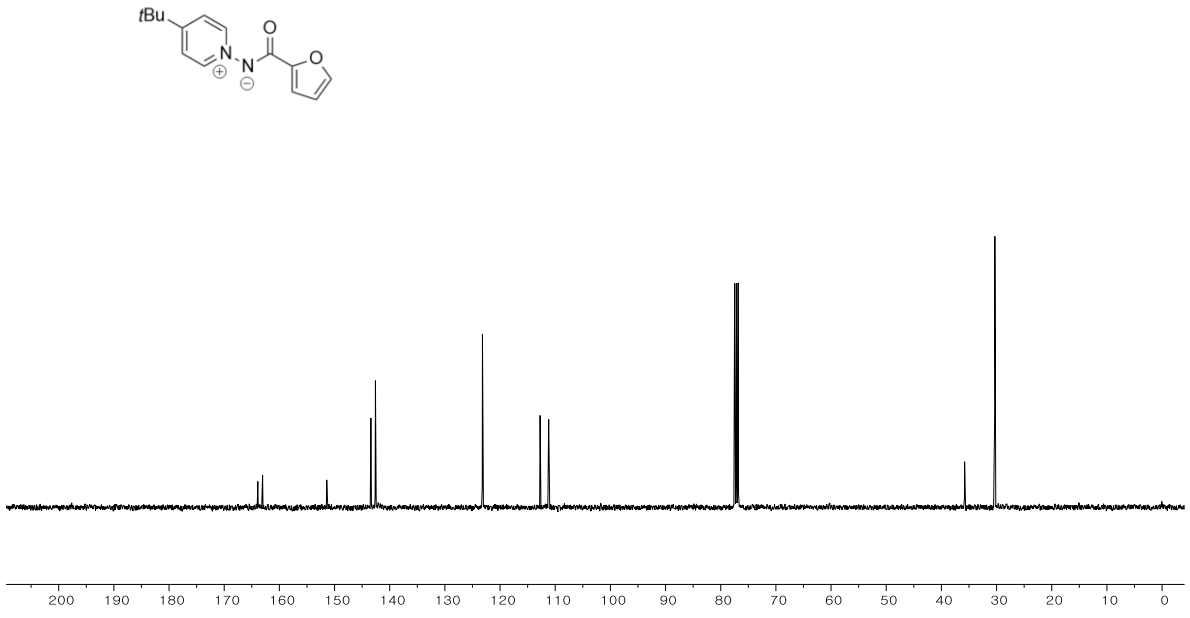
(4-(tert-Butyl)pyridin-1-ium-1-yl)(thiophene-3-carbonyl)amide



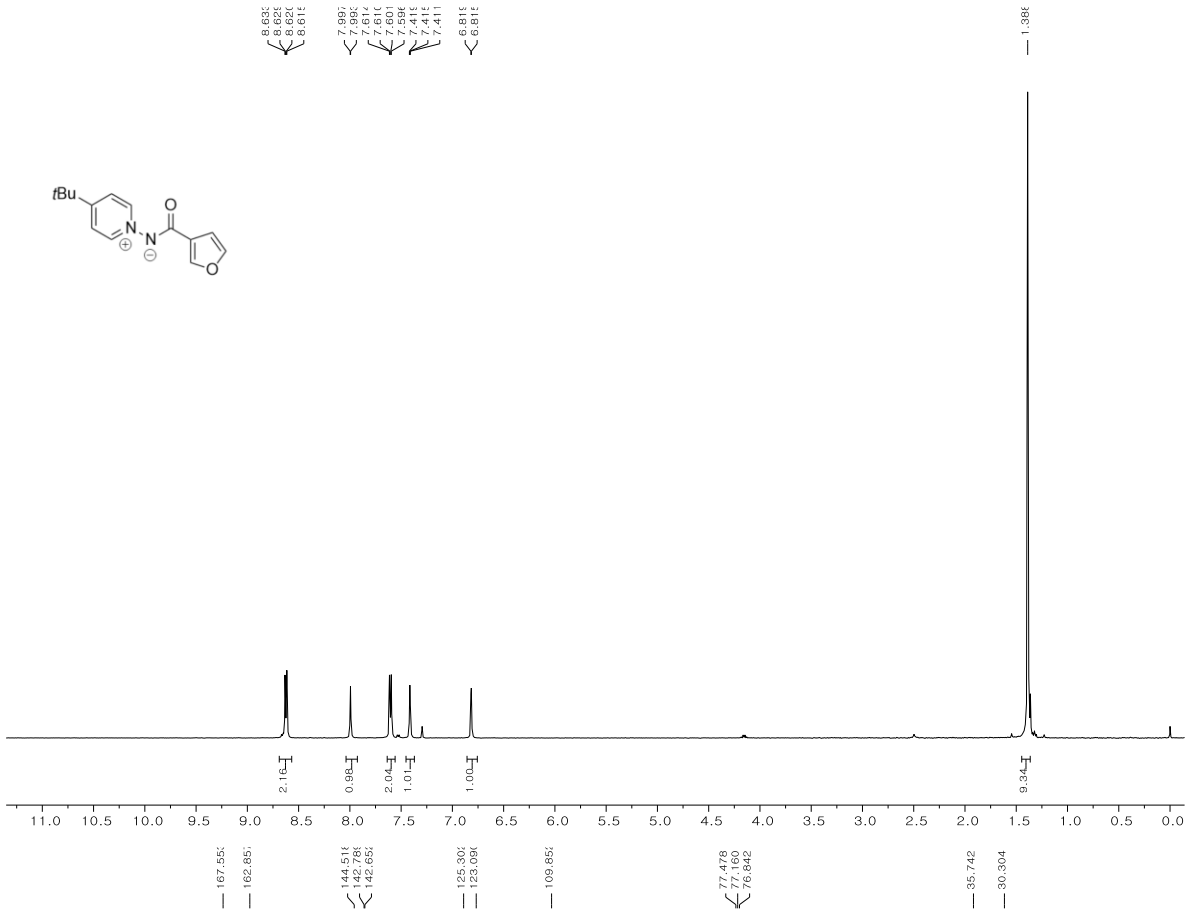


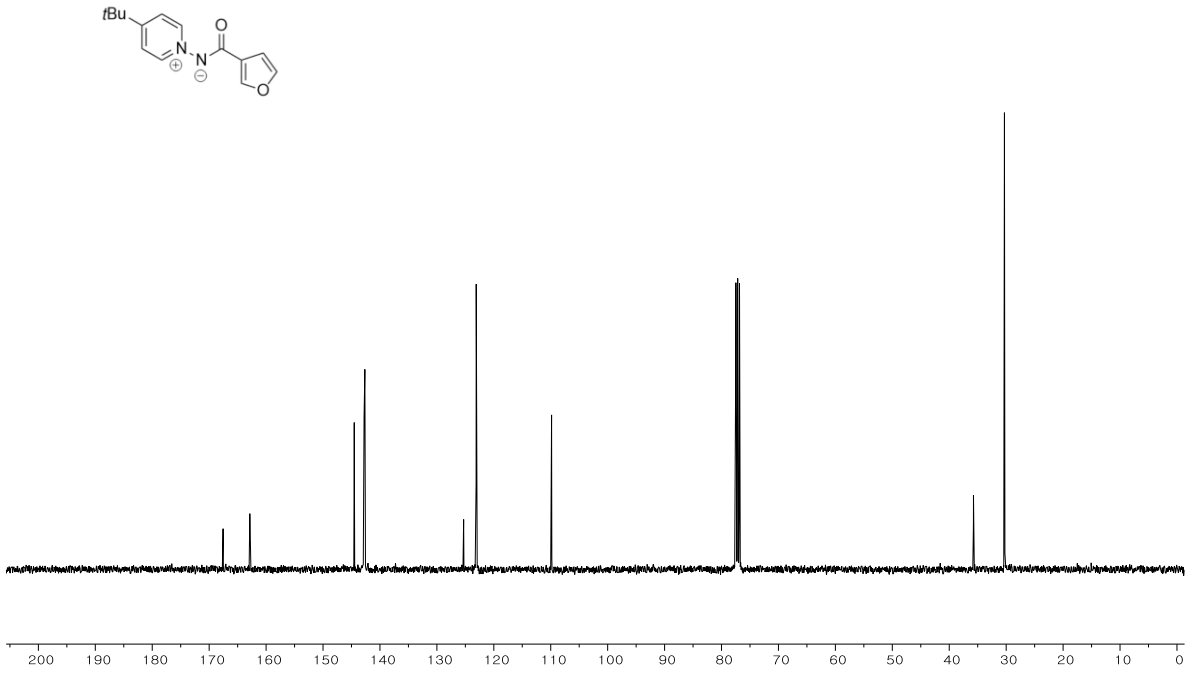
(4-(tert-Butyl)pyridin-1-ium-1-yl)(furan-2-carbonyl)amide



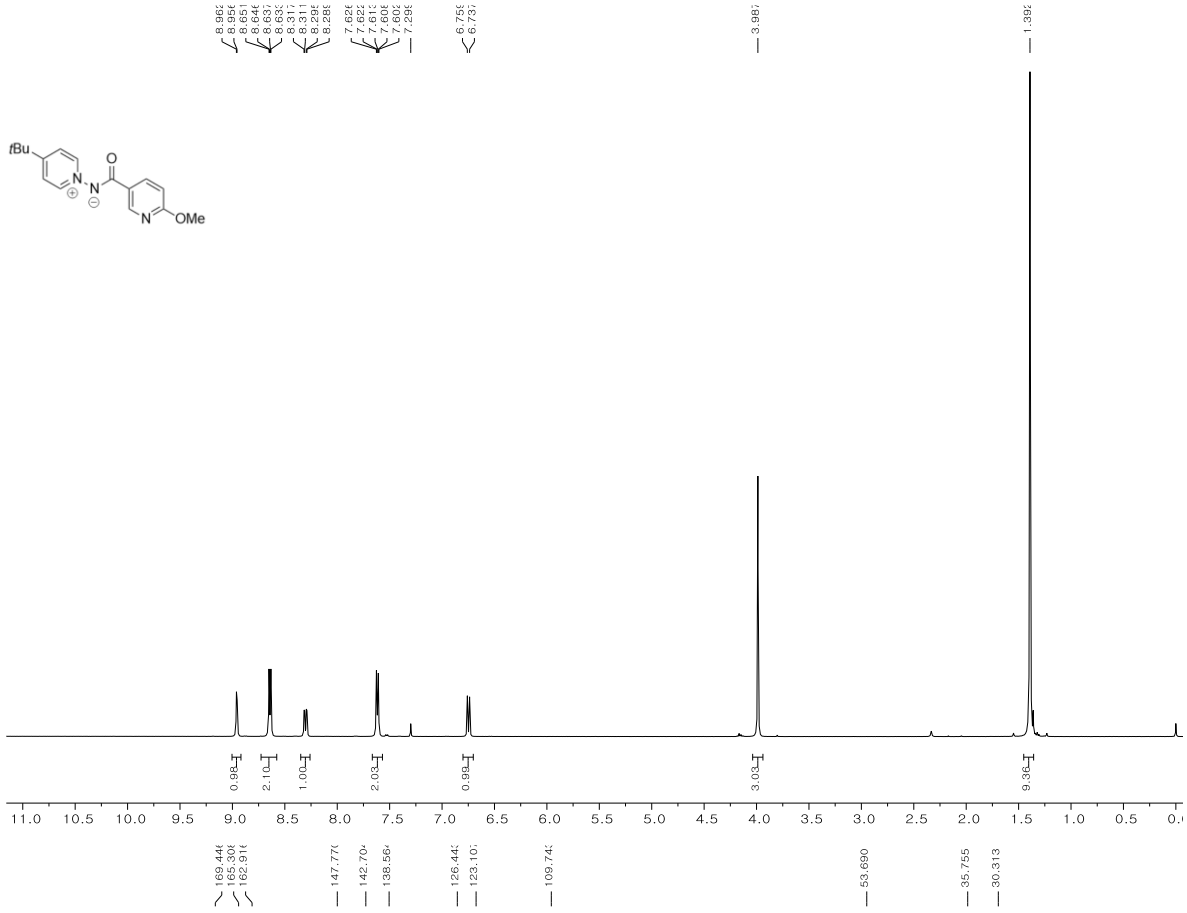


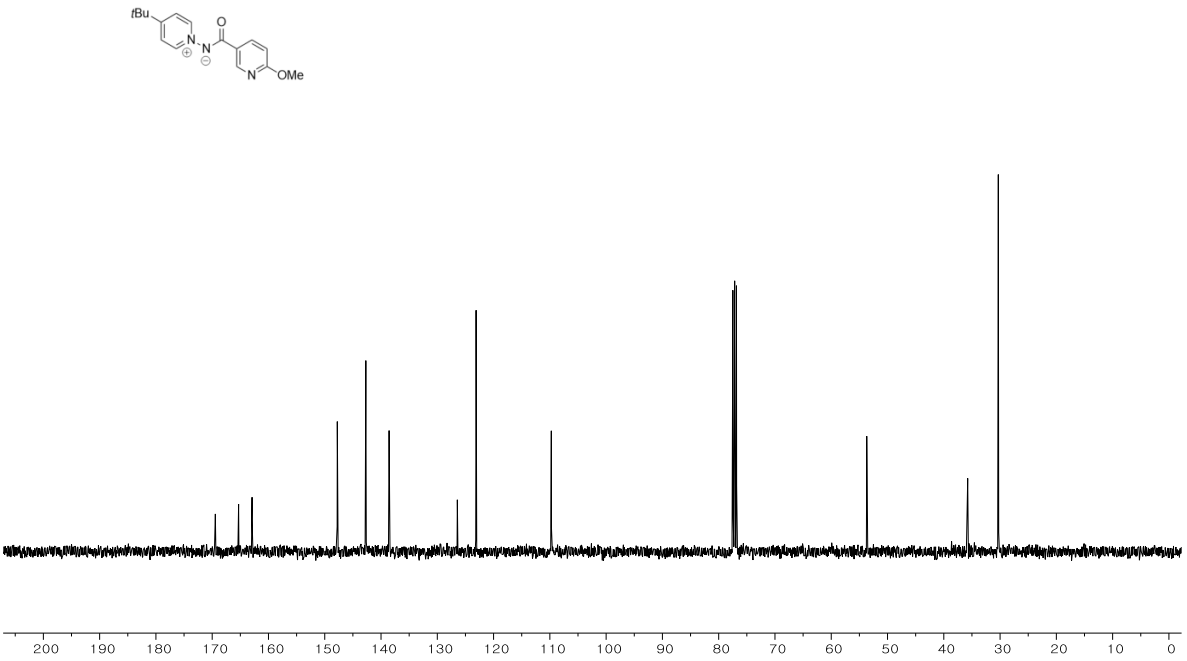
(4-(tert-Butyl)pyridin-1-ium-1-yl)(furan-3-carbonyl)amide



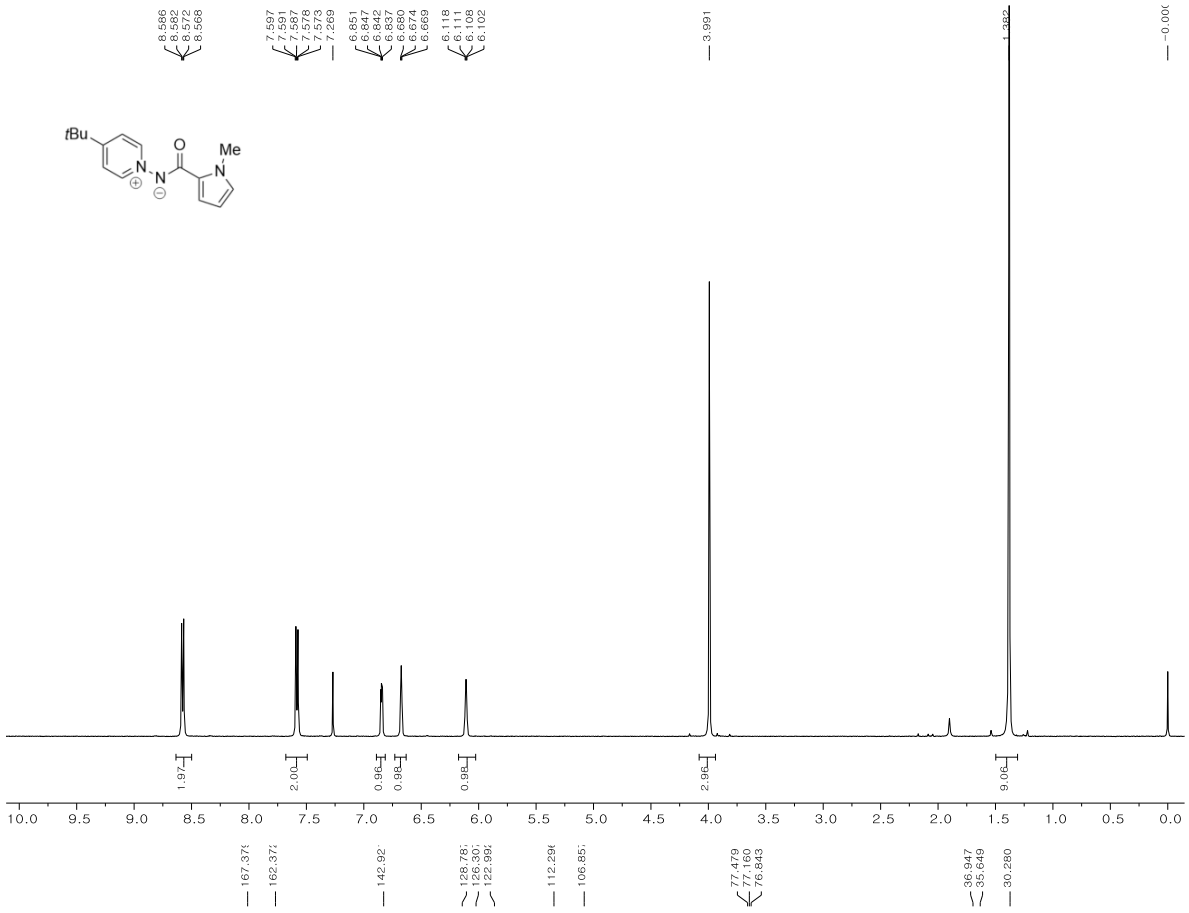


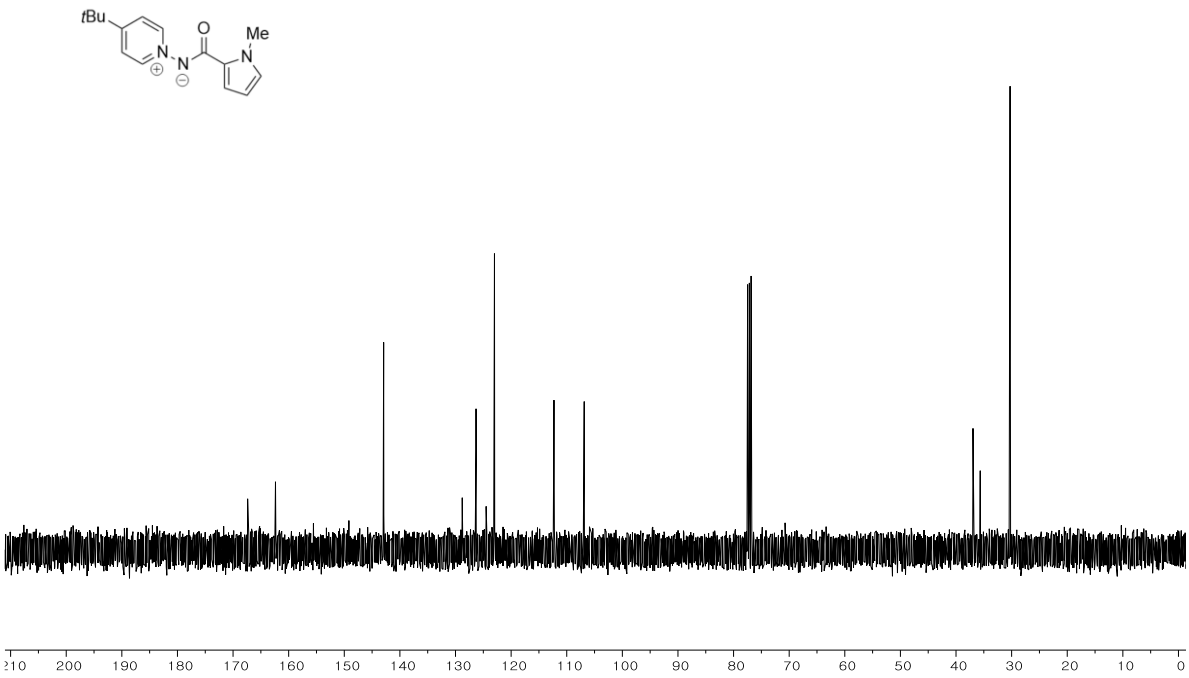
(4-(tert-Butyl)pyridin-1-ium-1-yl)(6-methoxynicotinoyl)amide



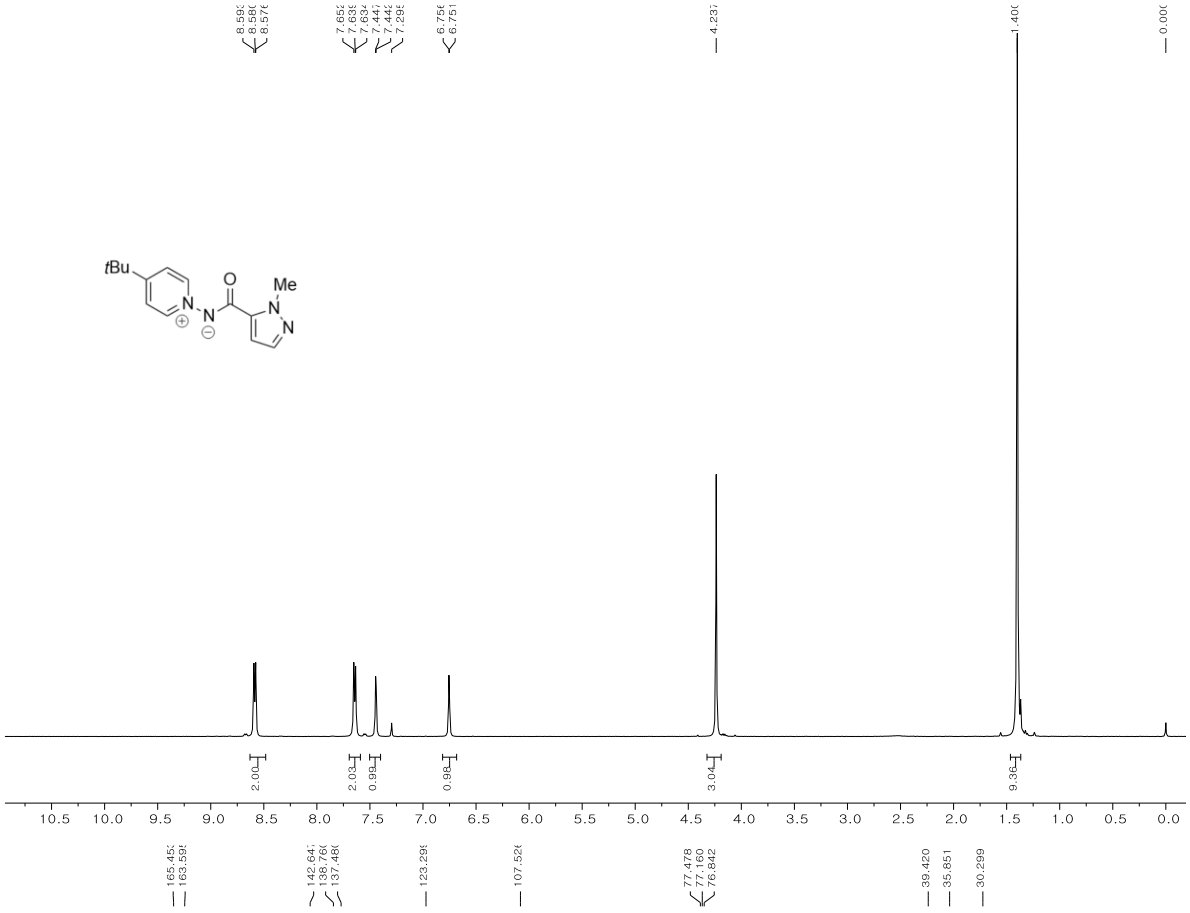


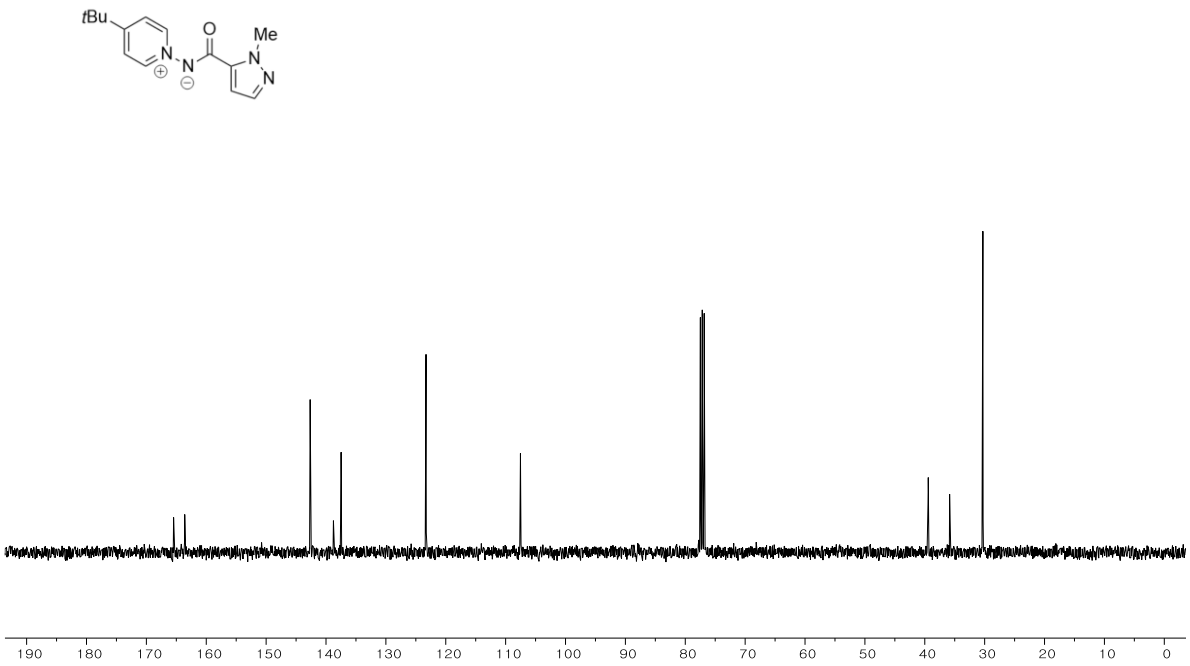
(4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-pyrrole-2-carbonyl)amide



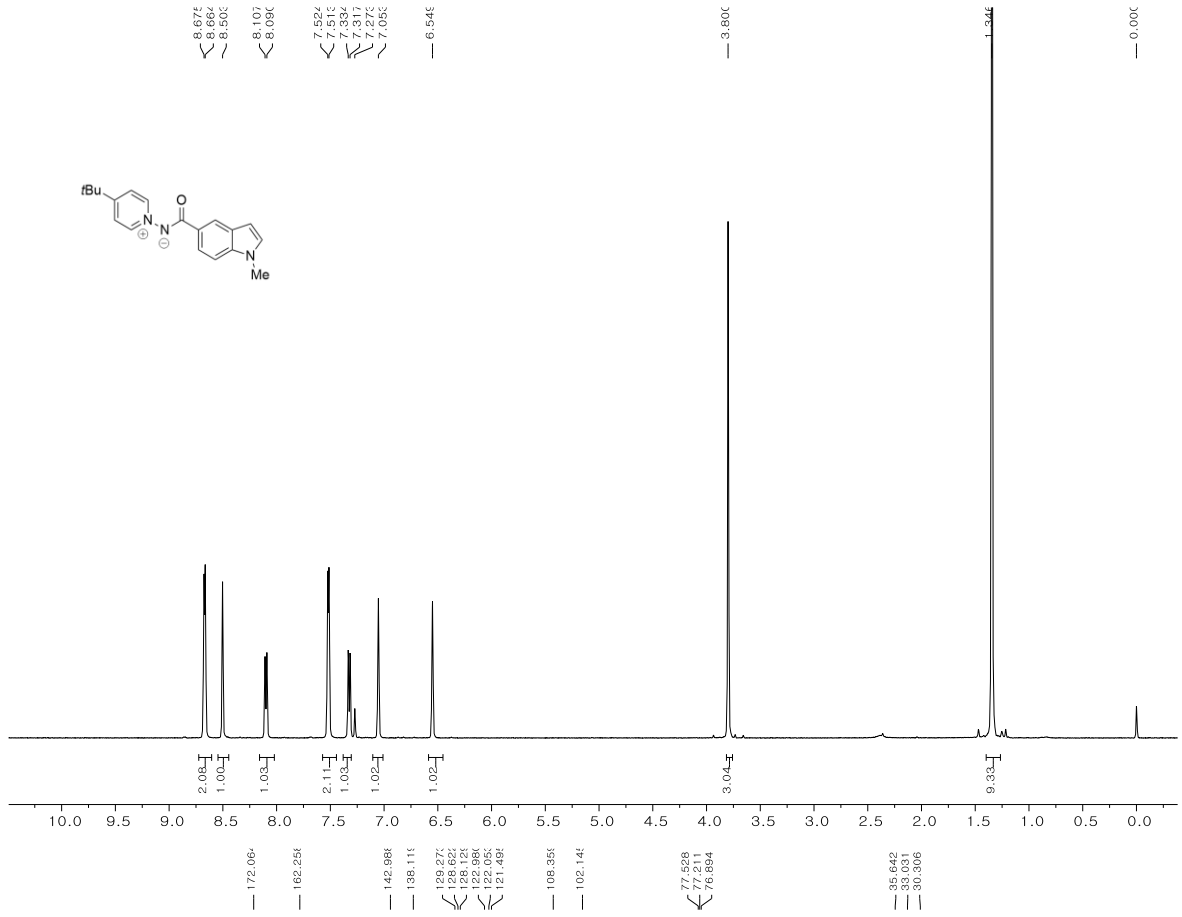


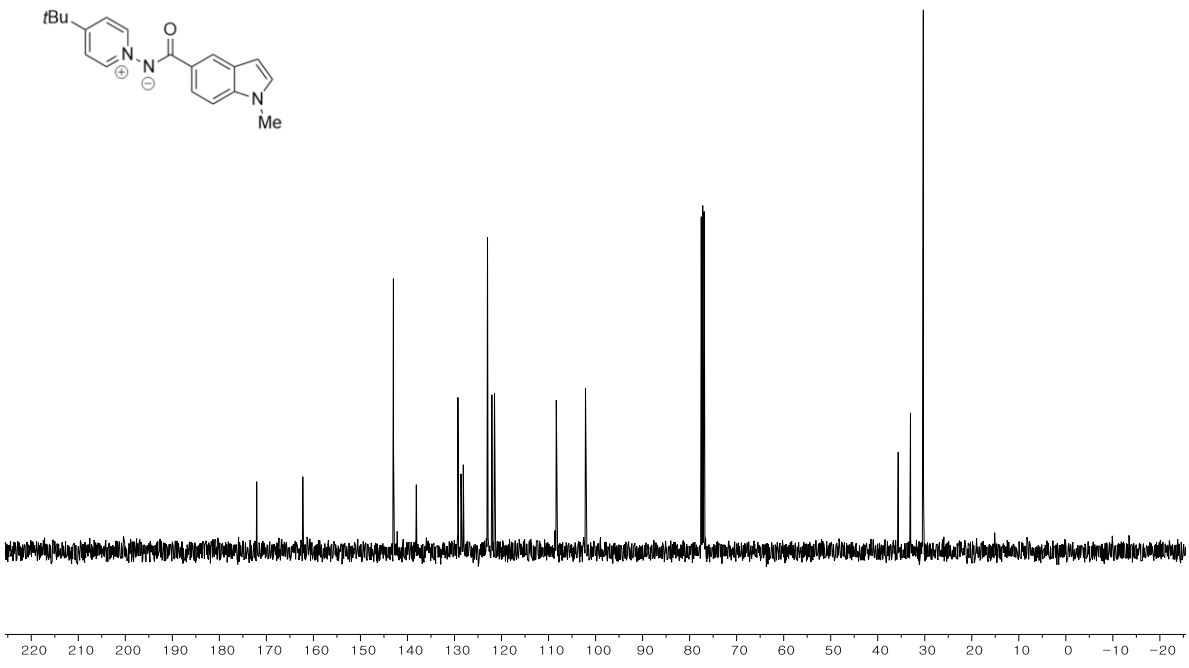
(4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-pyrazole-5-carbonyl)amide



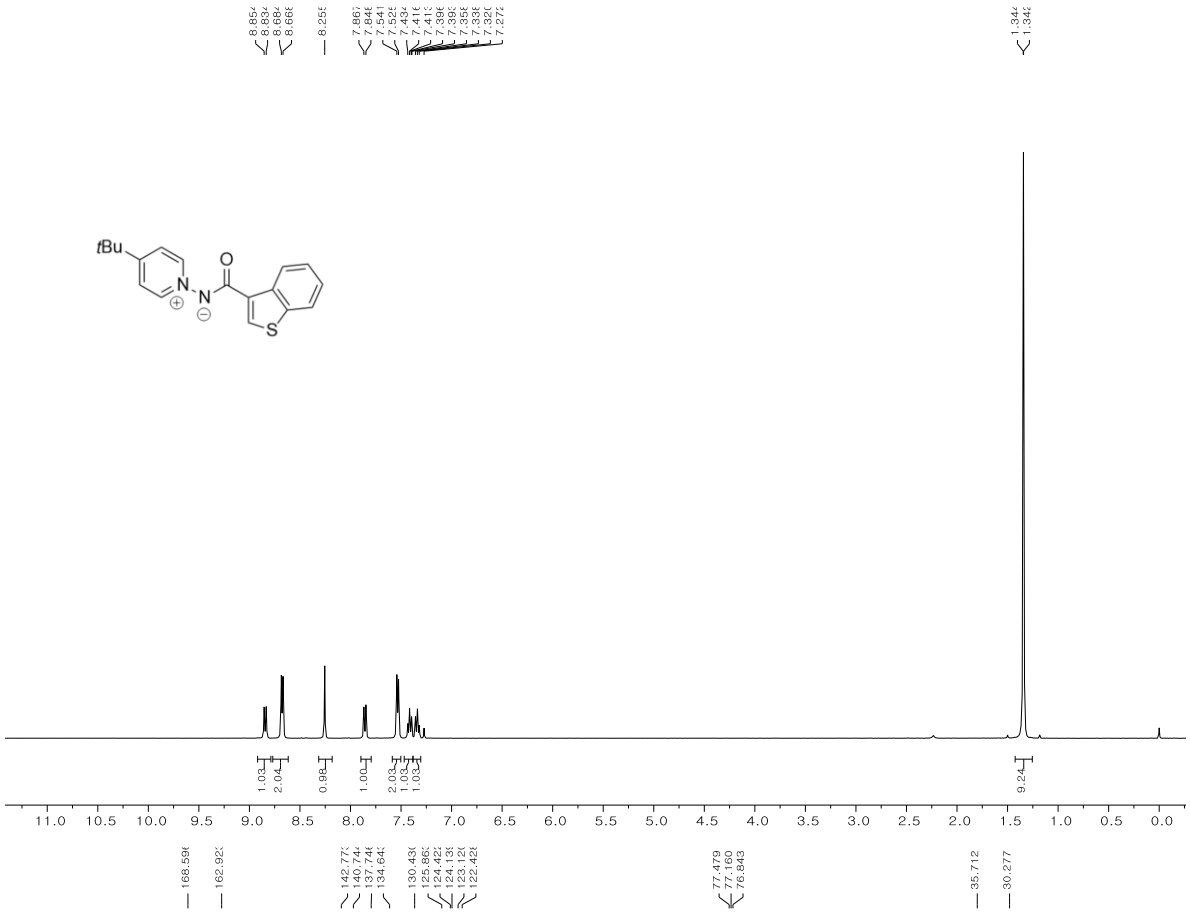


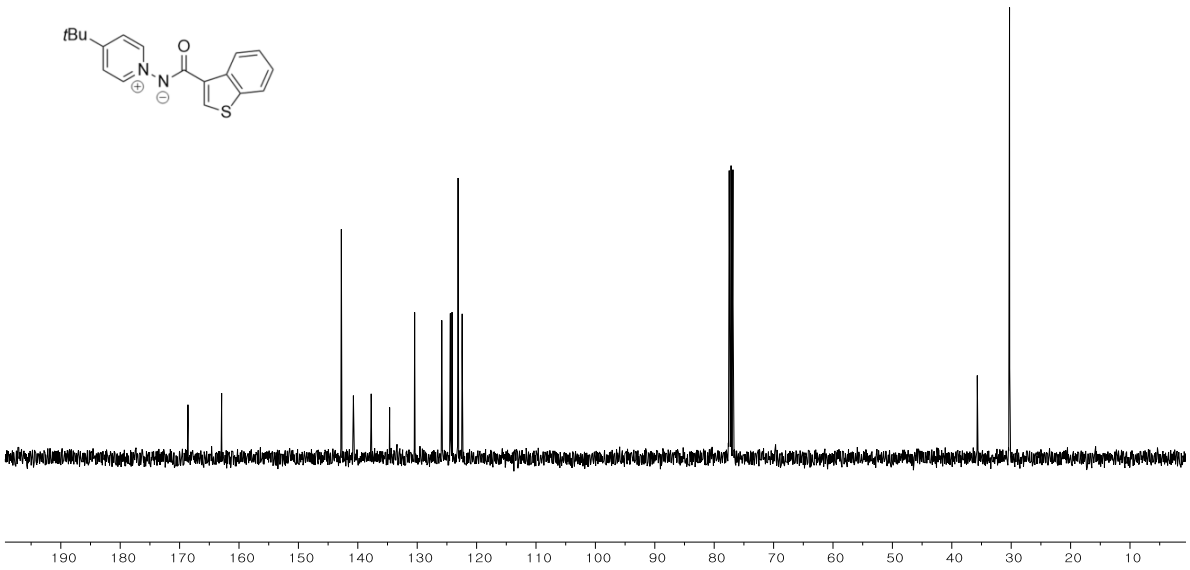
(4-(tert-Butyl)pyridin-1-ium-1-yl)(1-methyl-1H-indole-5-carbonyl)amide



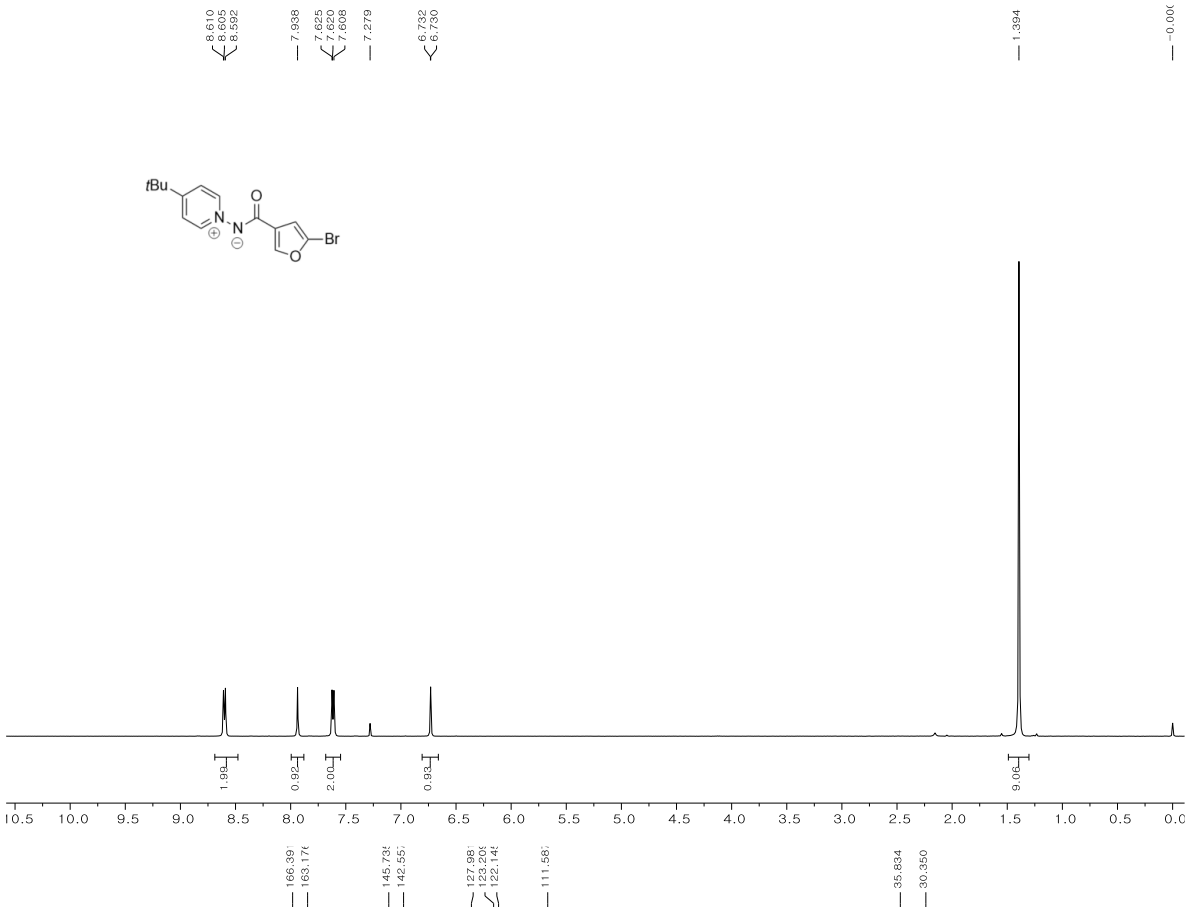


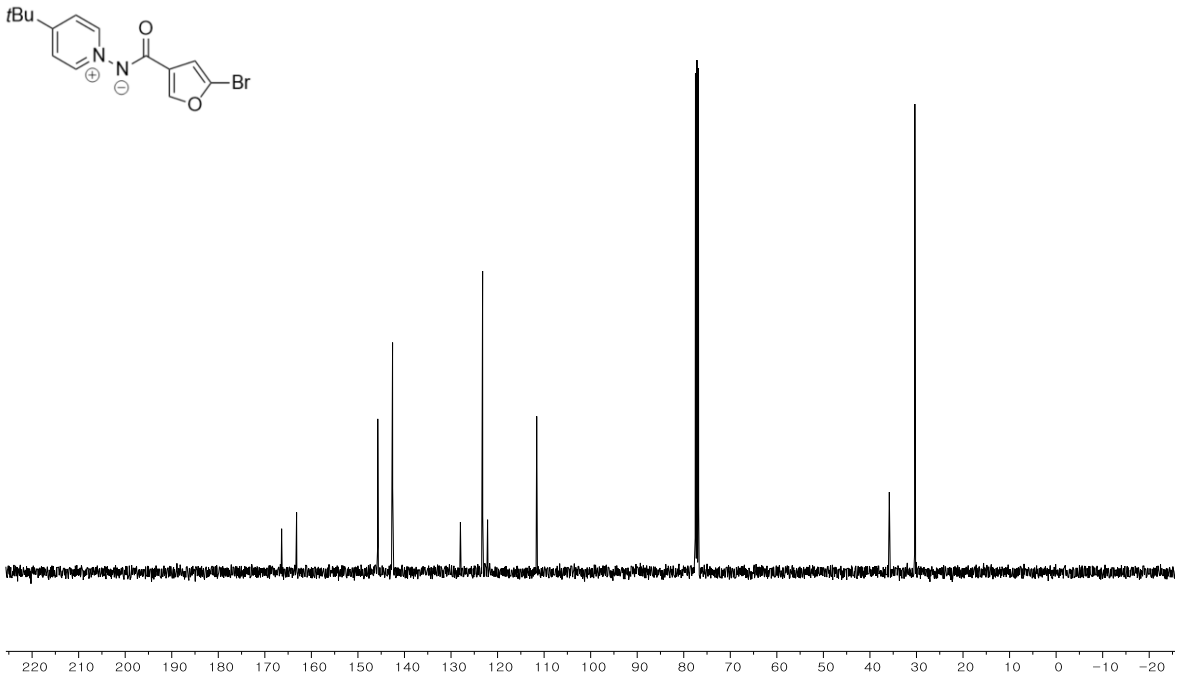
(Benzo[b]thiophene-3-carbonyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide



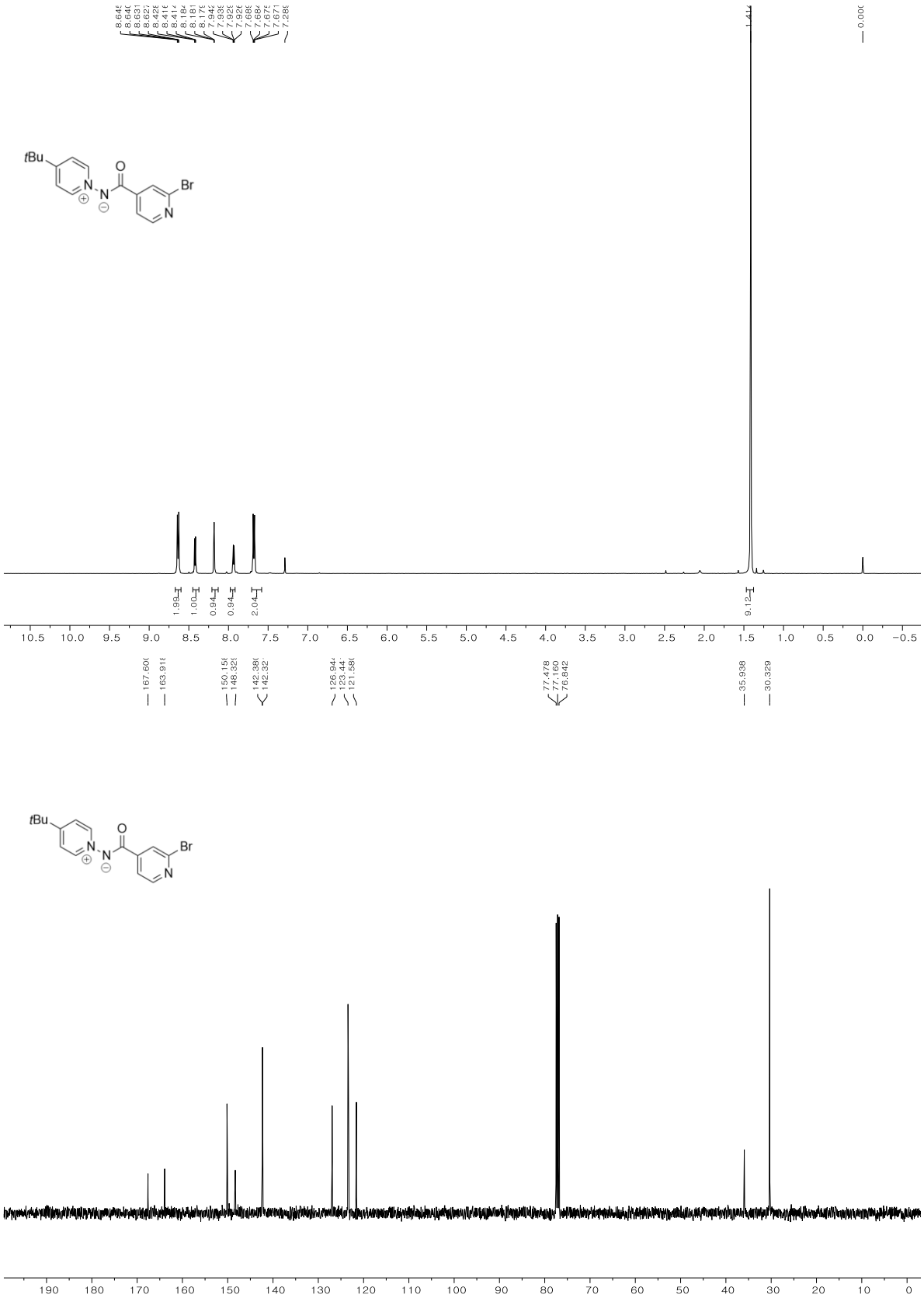


(5-Bromofuran-3-carbonyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide

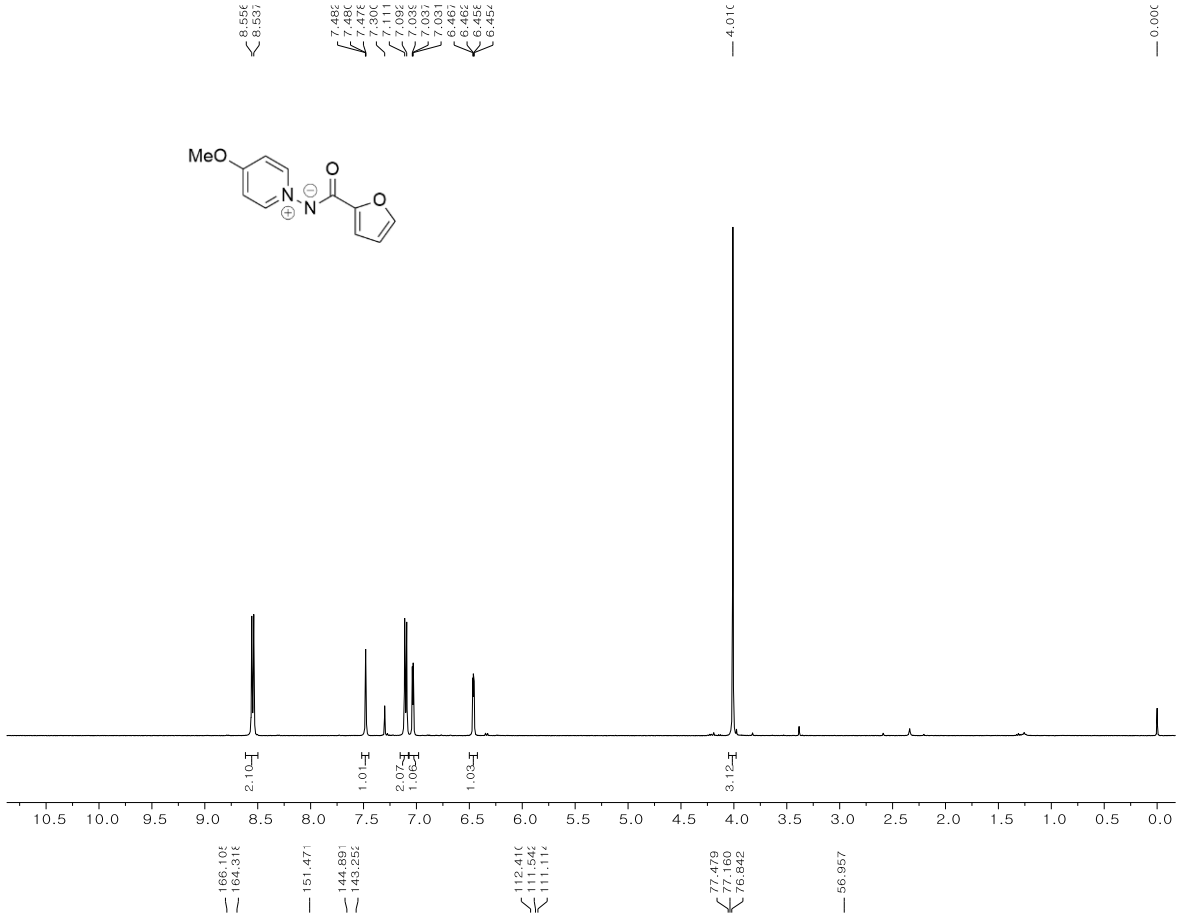


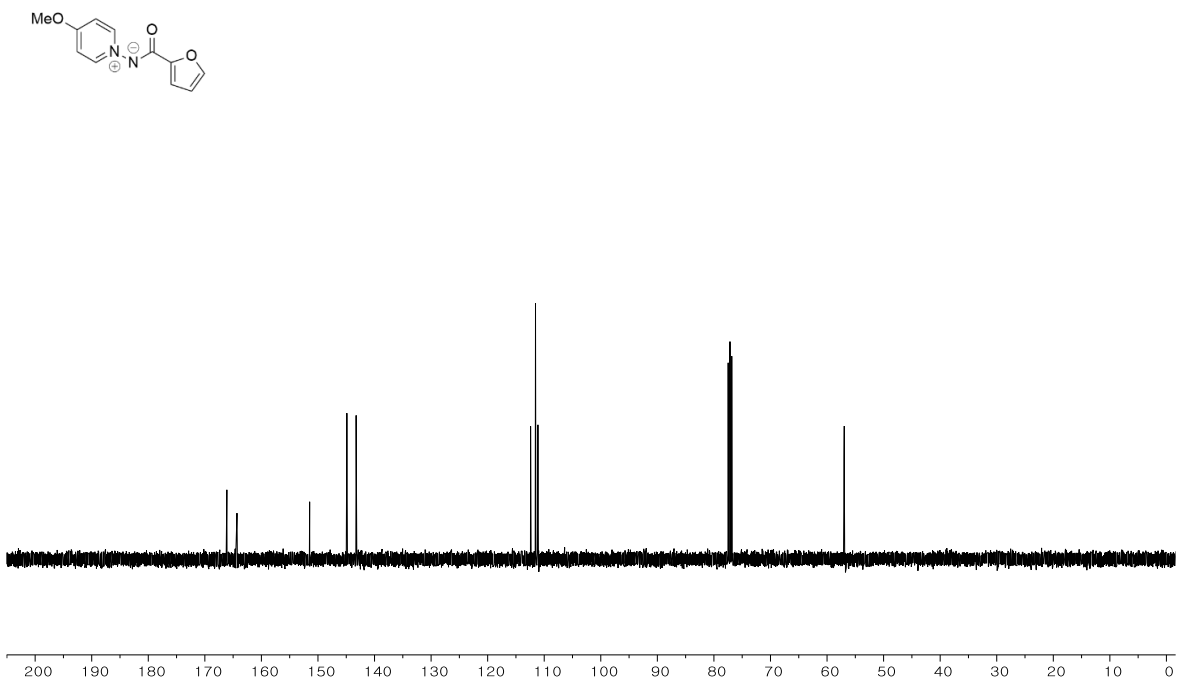


(2-Bromoisonicotinoyl)(4-(tert-butyl)pyridin-1-ium-1-yl)amide

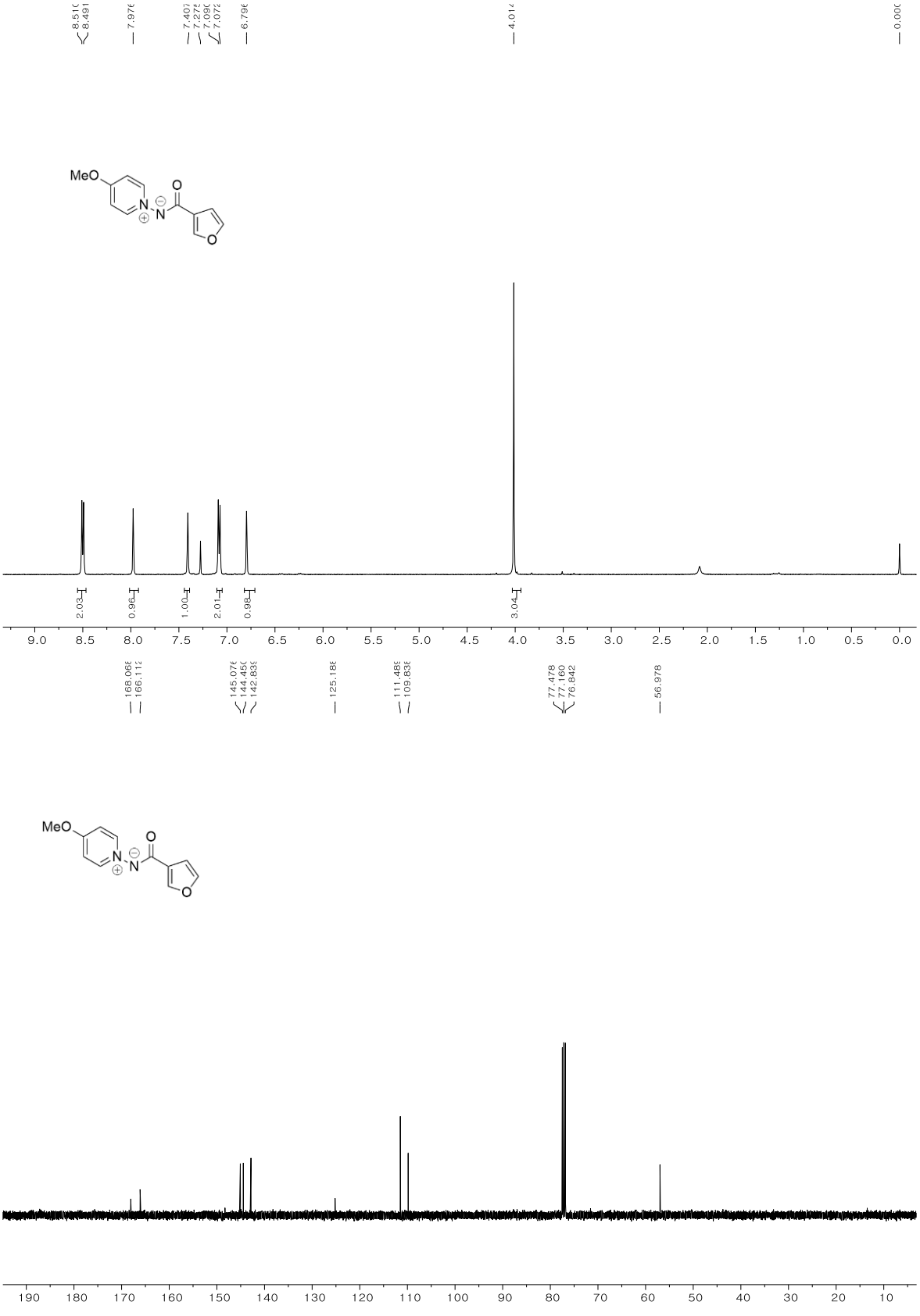


(Furan-2-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide

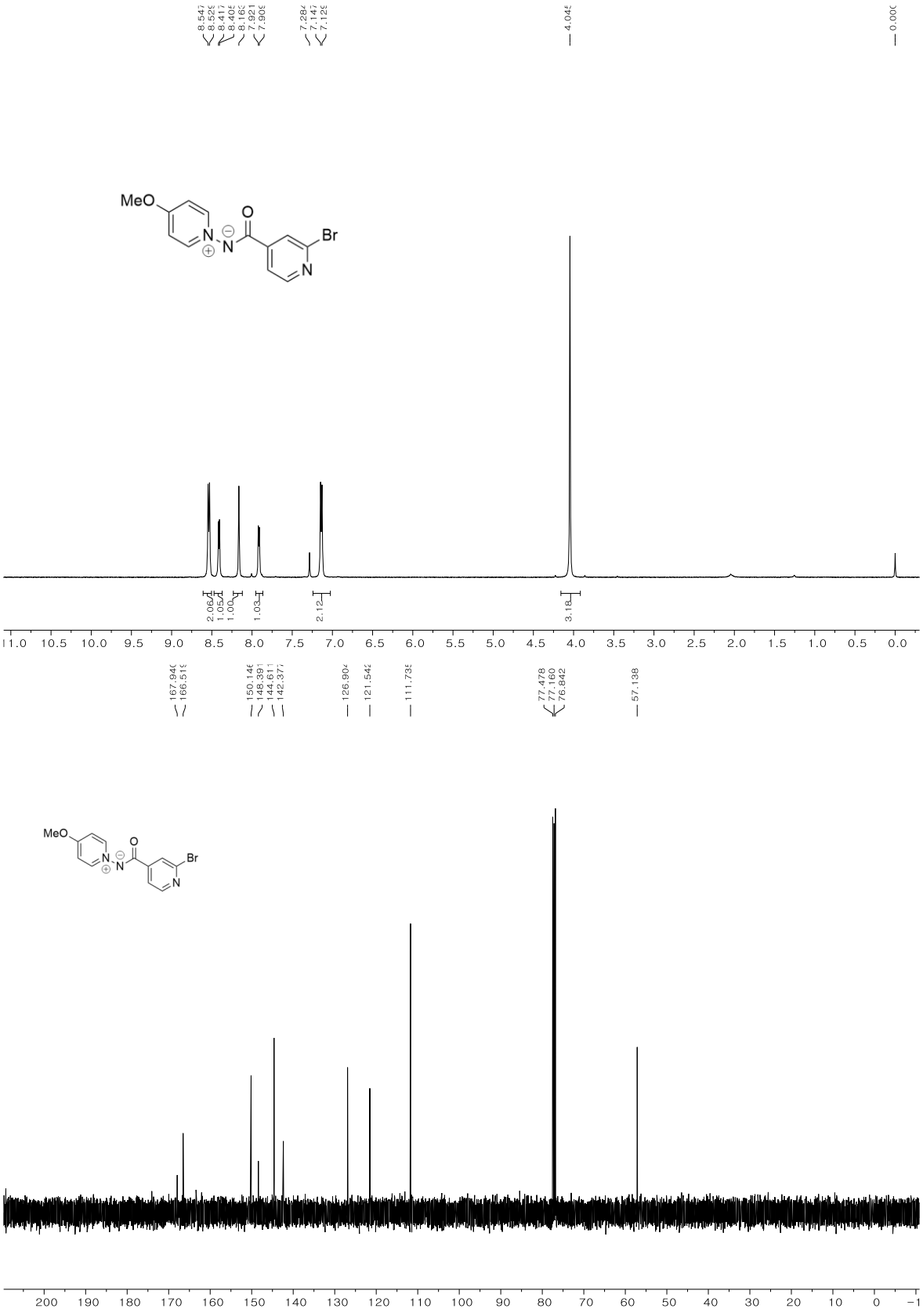




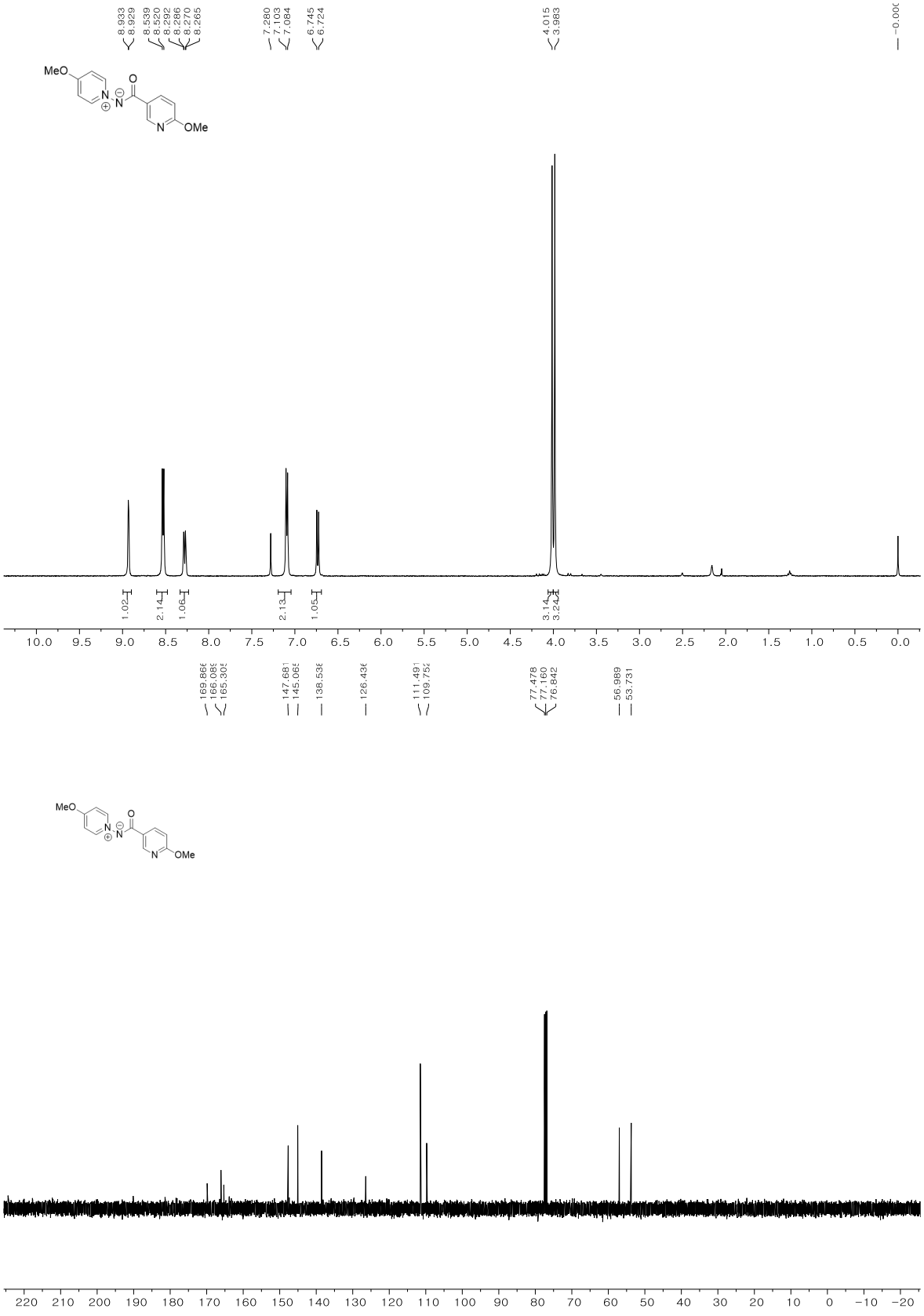
(Furan-3-carbonyl)(4-methoxypyridin-1-ium-1-yl)amide



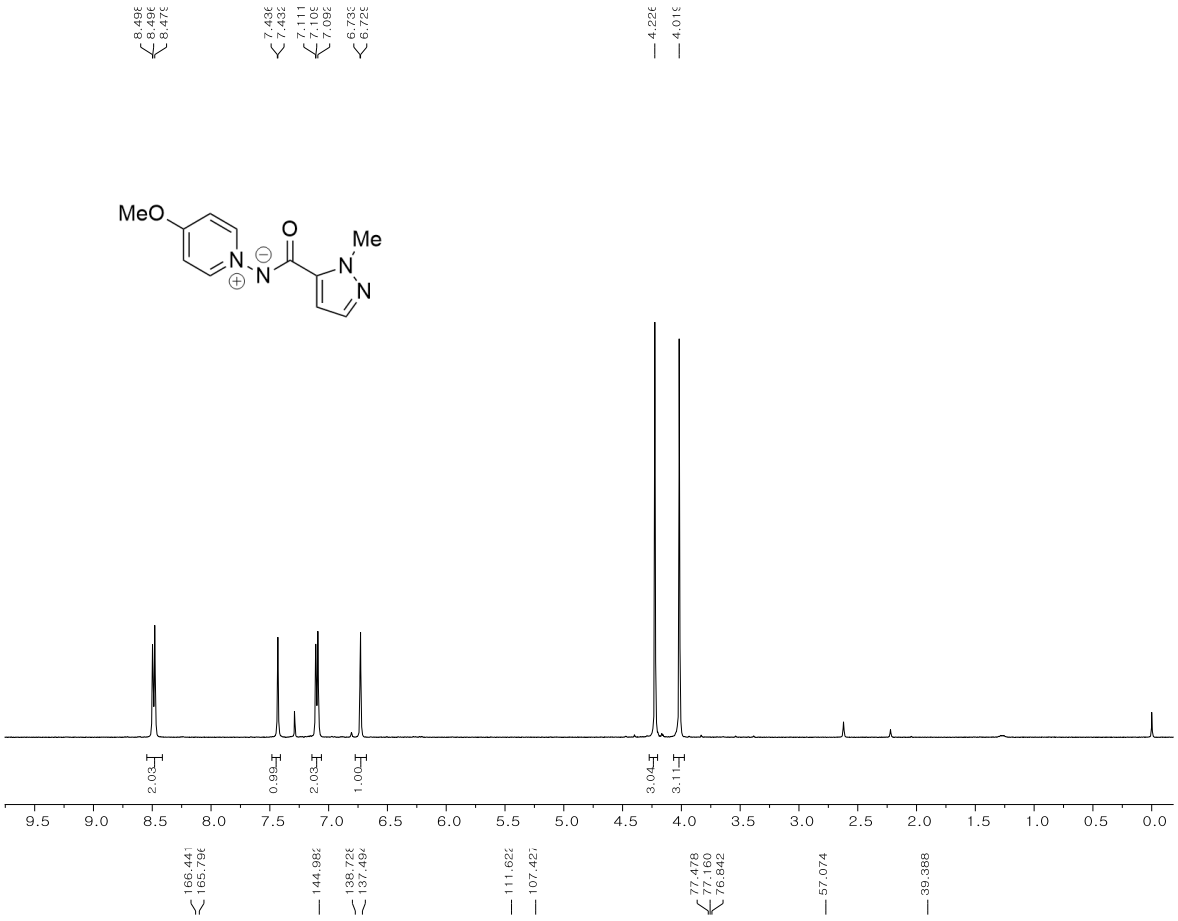
(2-Bromoisonicotinoyl)(4-methoxypyridin-1-ium-1-yl)amide

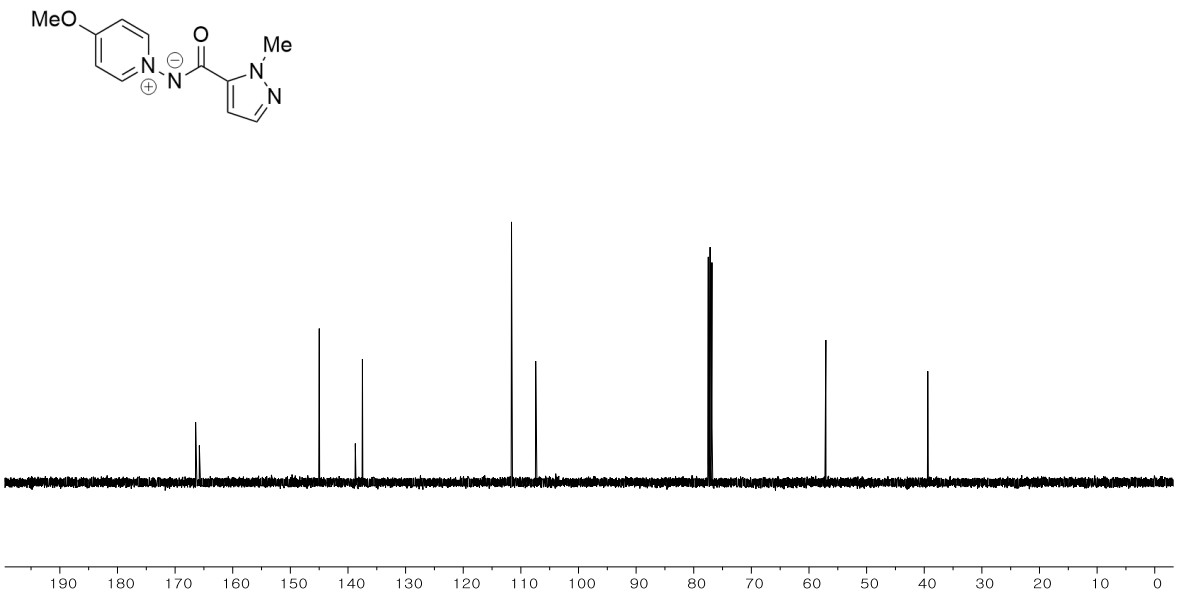


(6-Methoxynicotinoyl)(4-methoxypyridin-1-ium-1-yl)amide

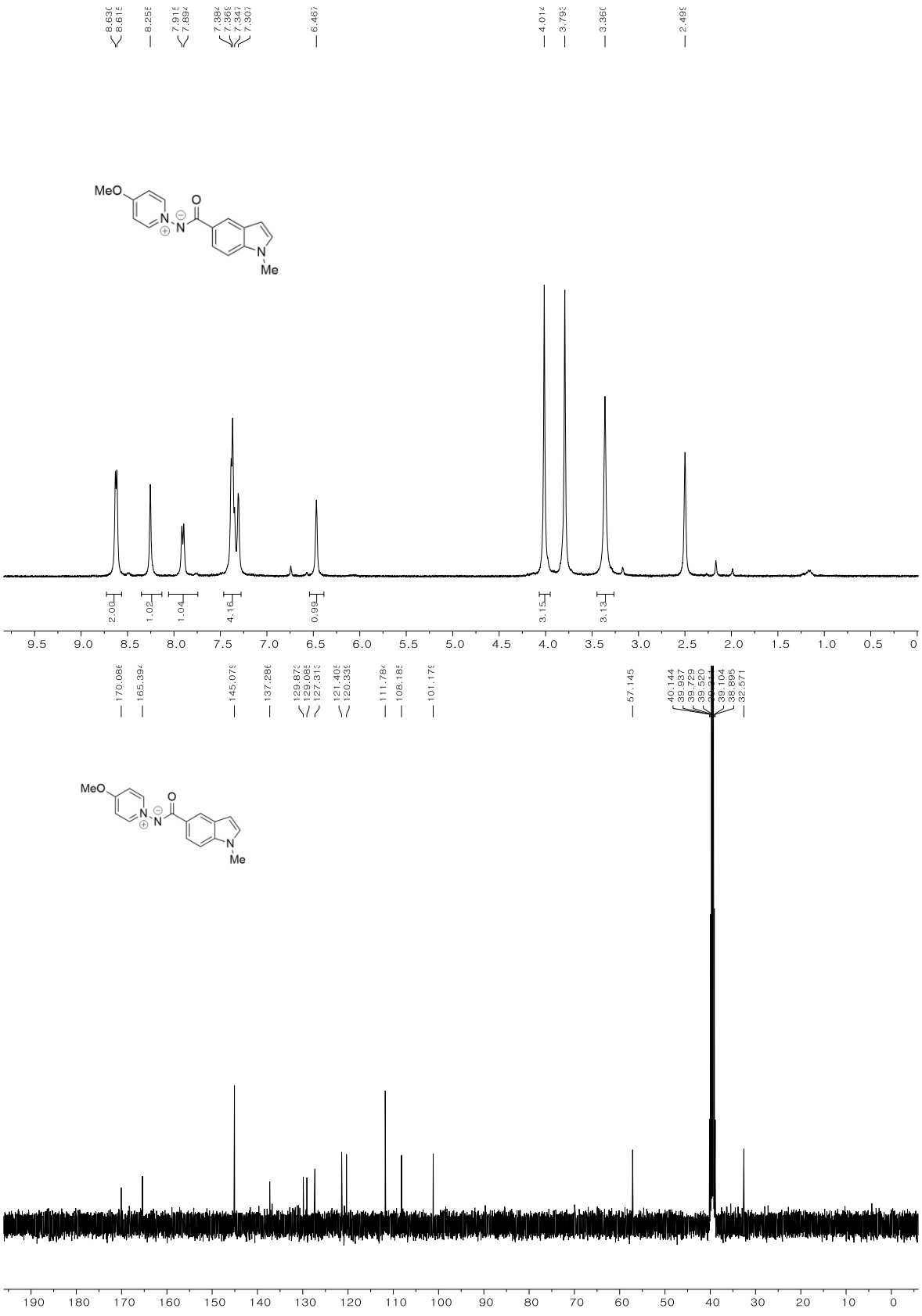


(4-Methoxypyridin-1-ium-1-yl)(1-methyl-1H-pyrazole-5-carbonyl)amide

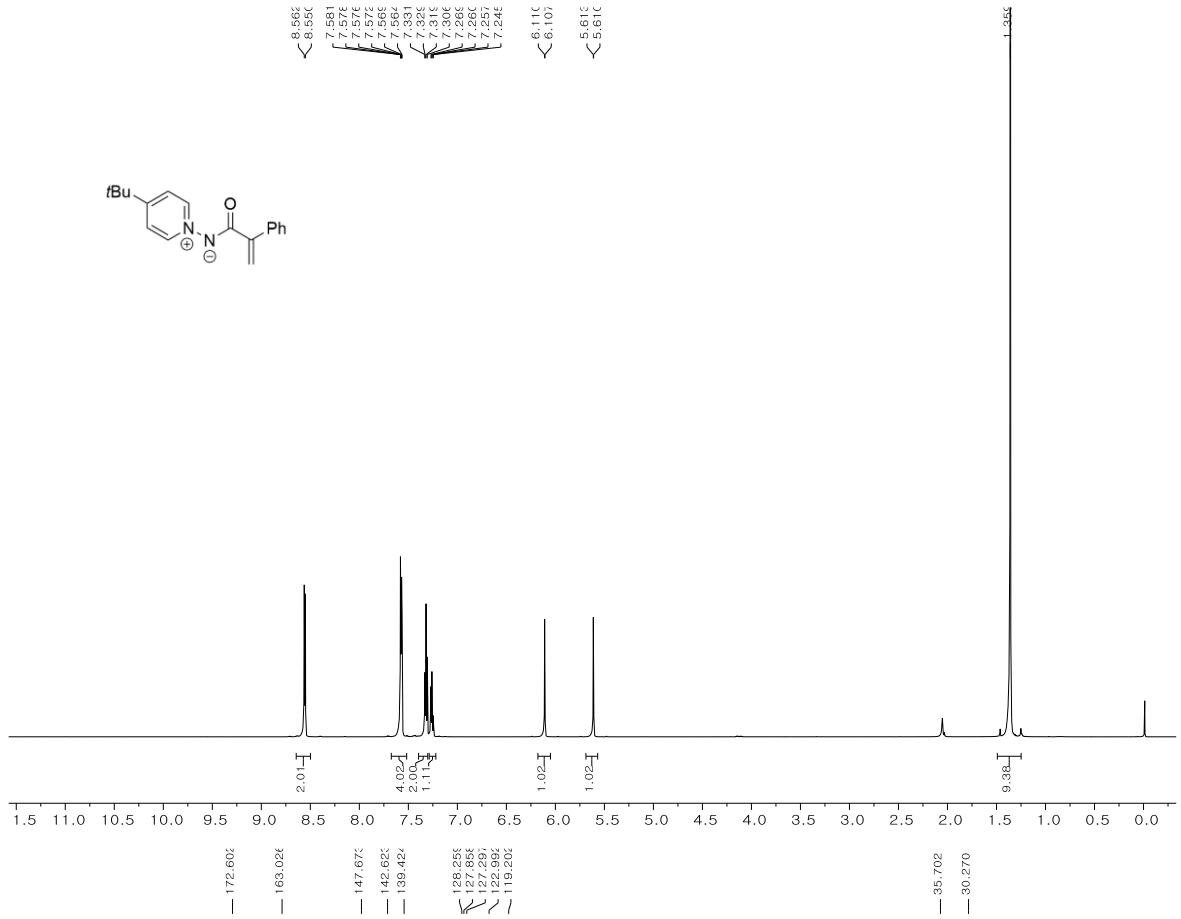


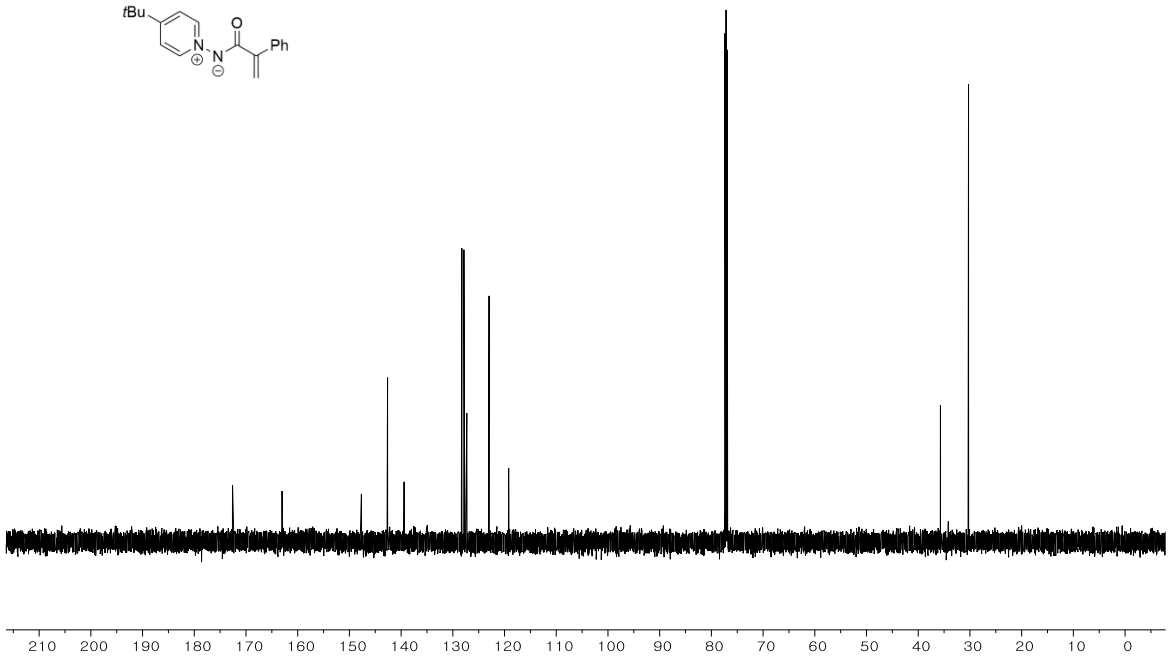


(4-Methoxypyridin-1-ium-1-yl)(1-methyl-1H-indole-5-carbonyl)amide

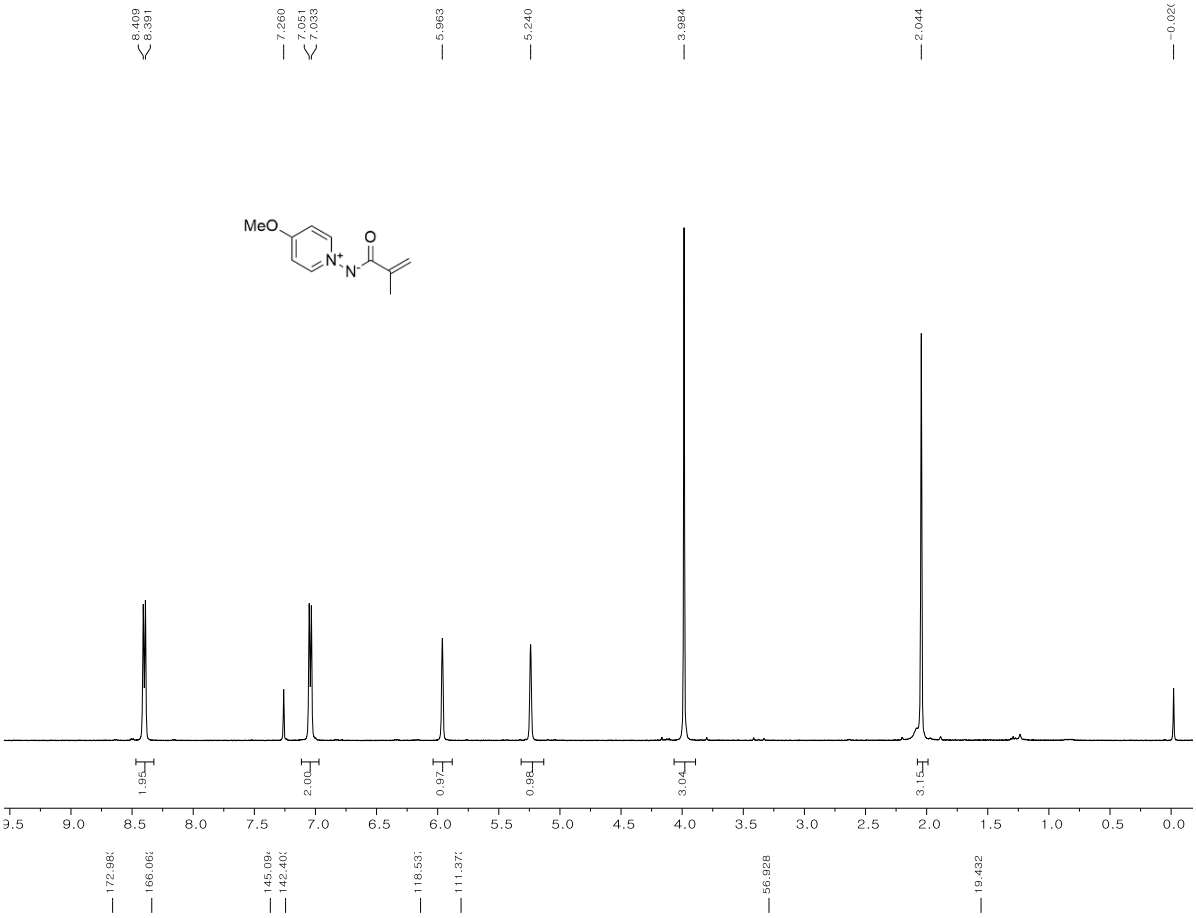


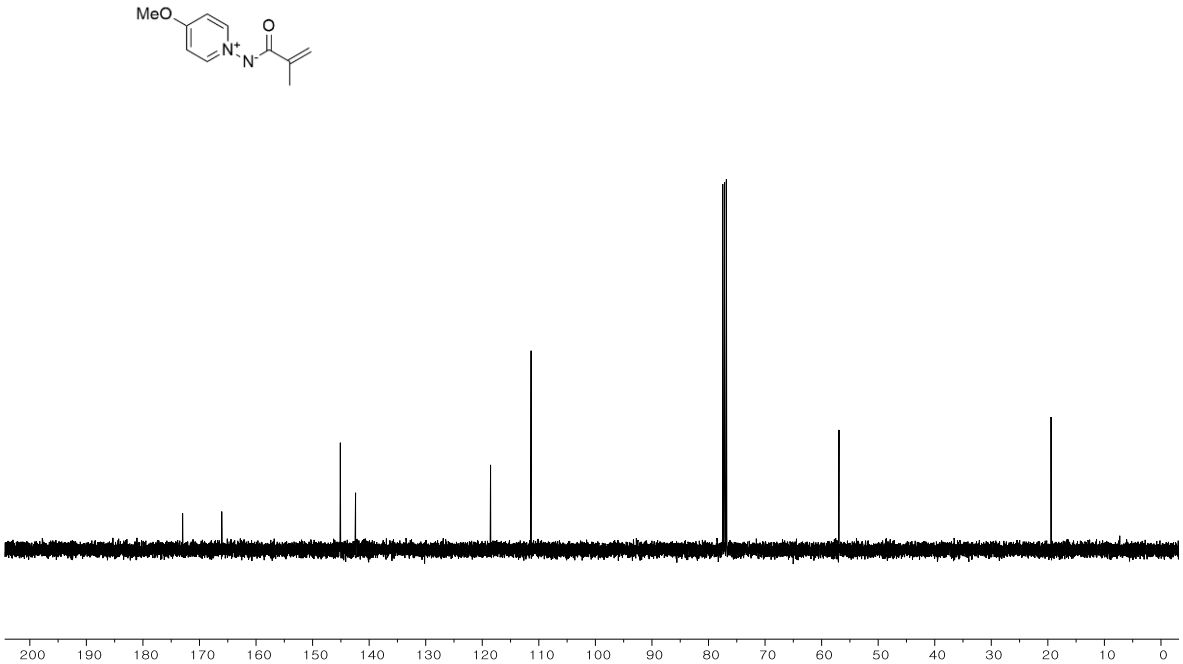
(4-(tert-butyl)pyridin-1-ium-1-yl)(2-phenylacryloyl)amide.



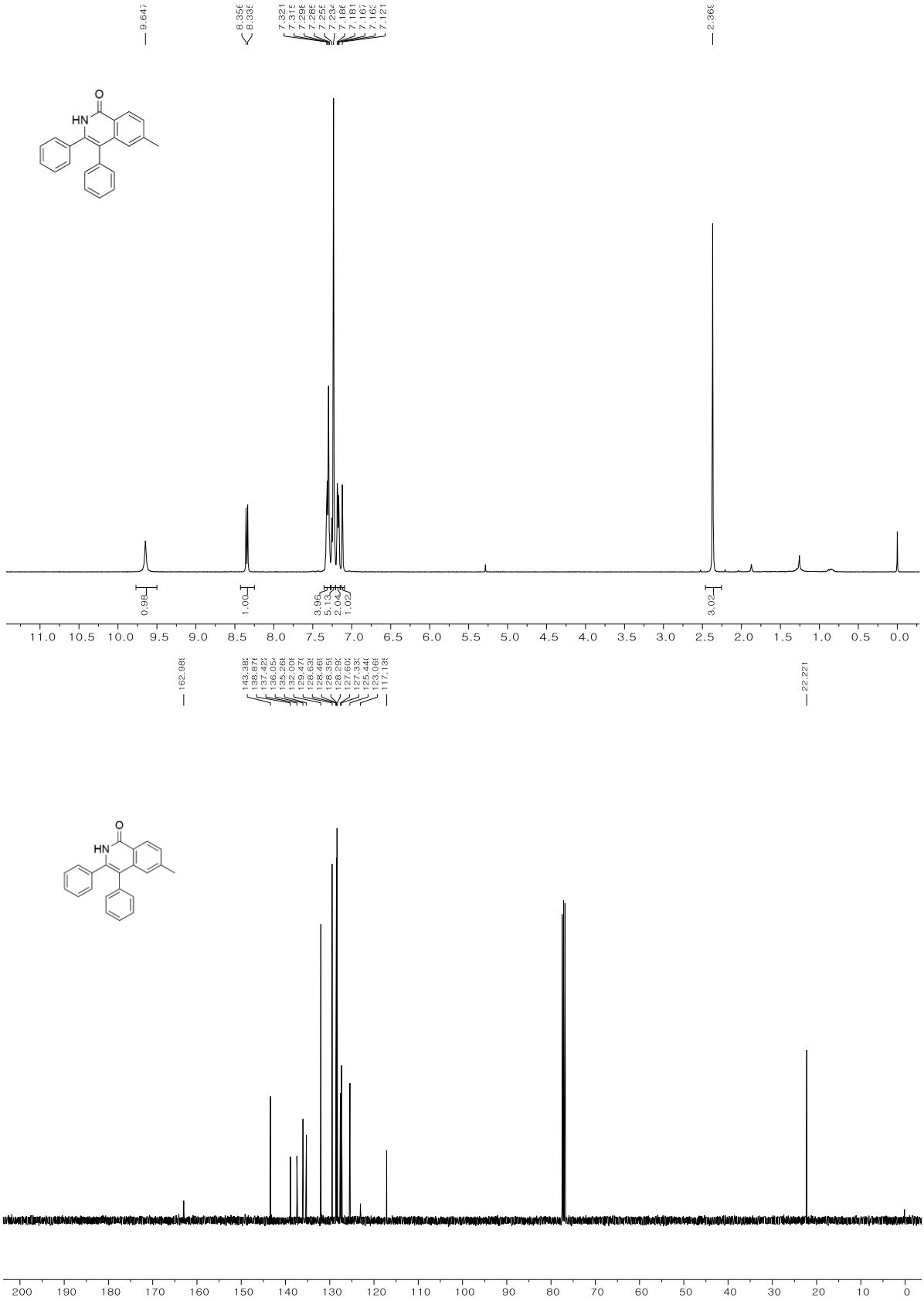


Methacryloyl(4-methoxypyridin-1-ium-1-yl)amide.

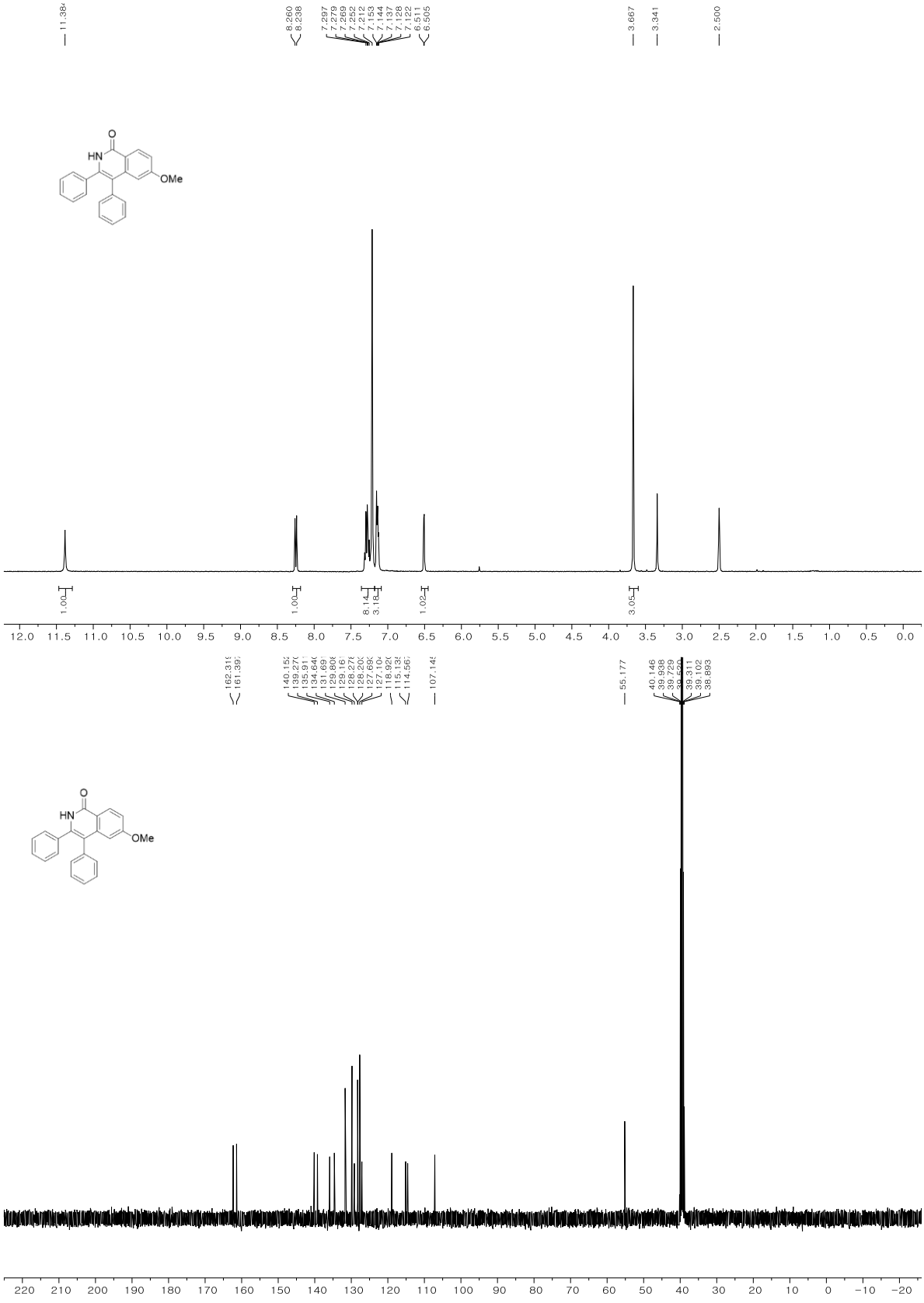




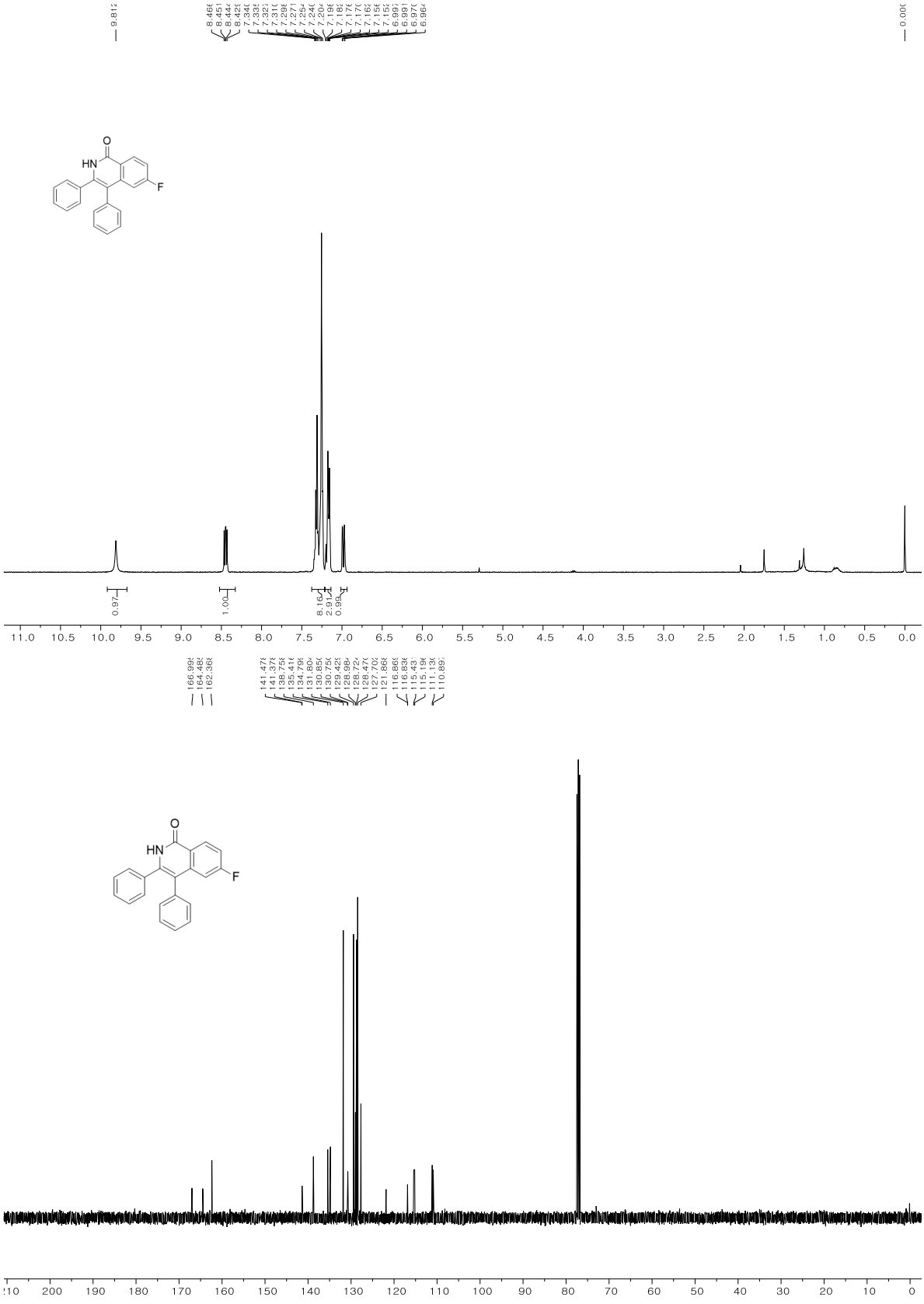
6-Methyl-3,4-diphenylisoquinolin-1(*2H*)-one (4)



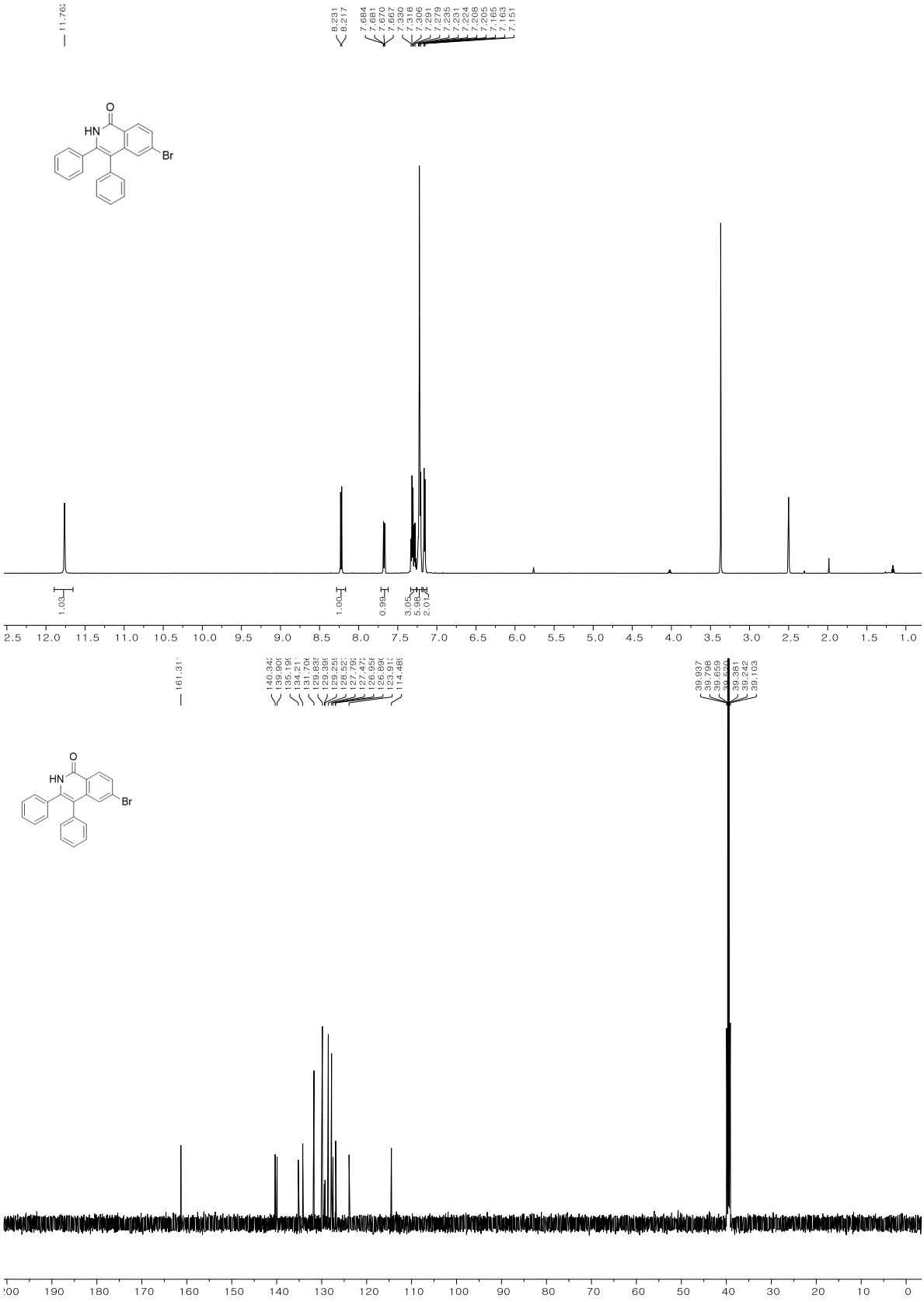
6-Methoxy-3,4-diphenylisoquinolin-1(2H)-one (5).



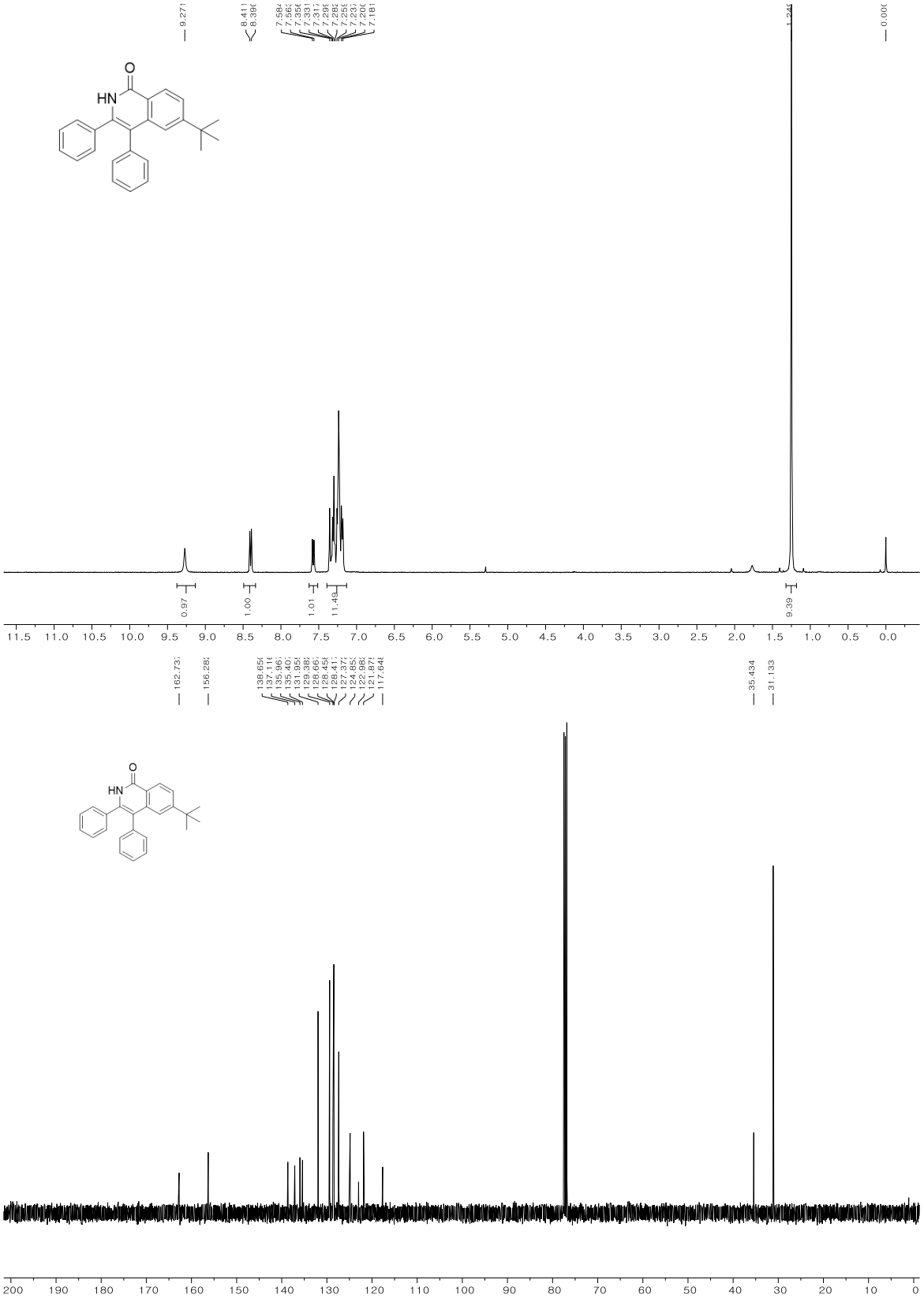
6-Fluoro-3,4-diphenylisoquinolin-1(*2H*)-one (6).



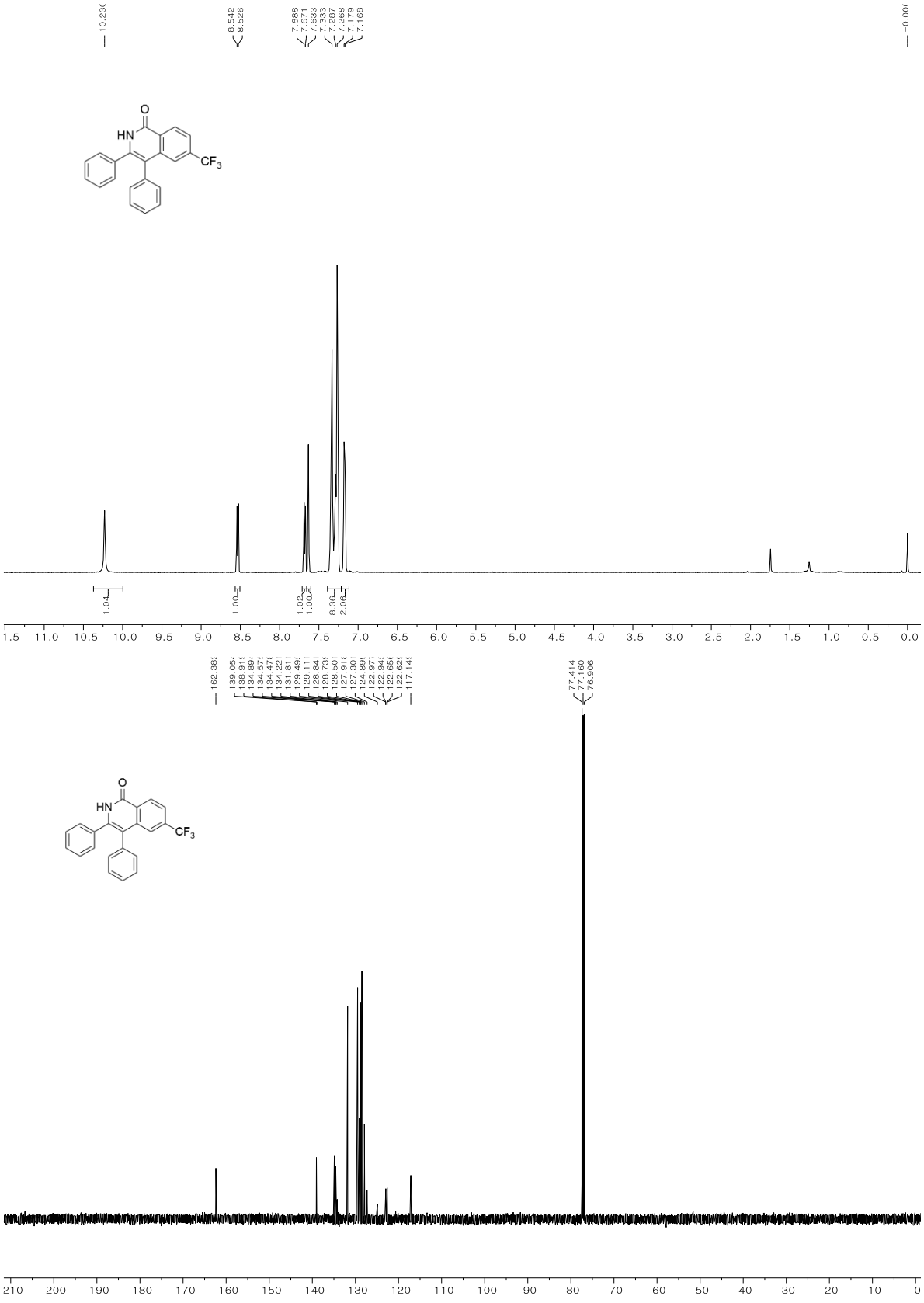
6-Bromo-3,4-diphenylisoquinolin-1(2H)-one (7).



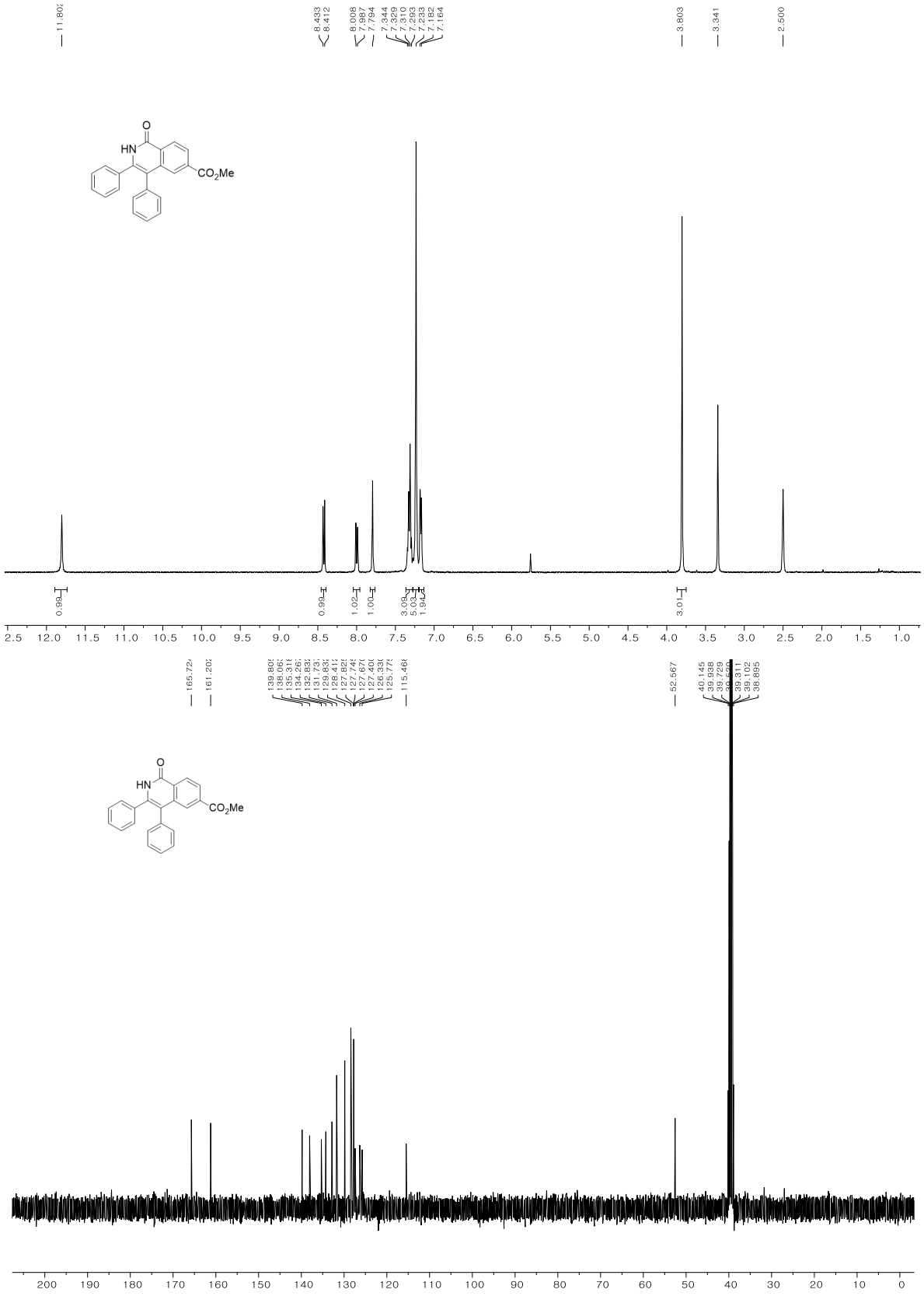
6-(tert-Butyl)-3,4-diphenylisoquinolin-1(*2H*)-one (8).



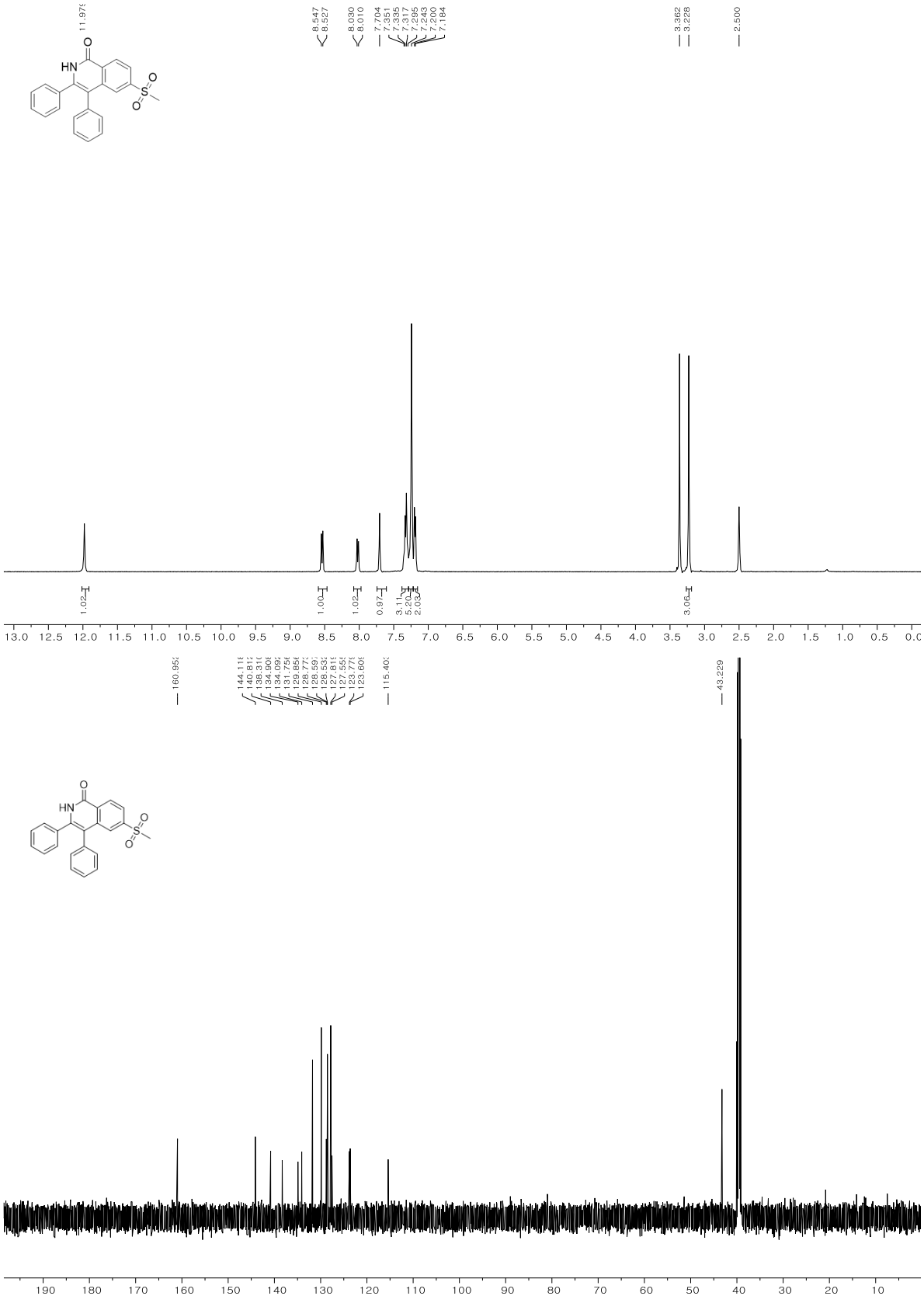
3,4-diphenyl-6-(trifluoromethyl)isoquinolin-1(2H)-one (9).



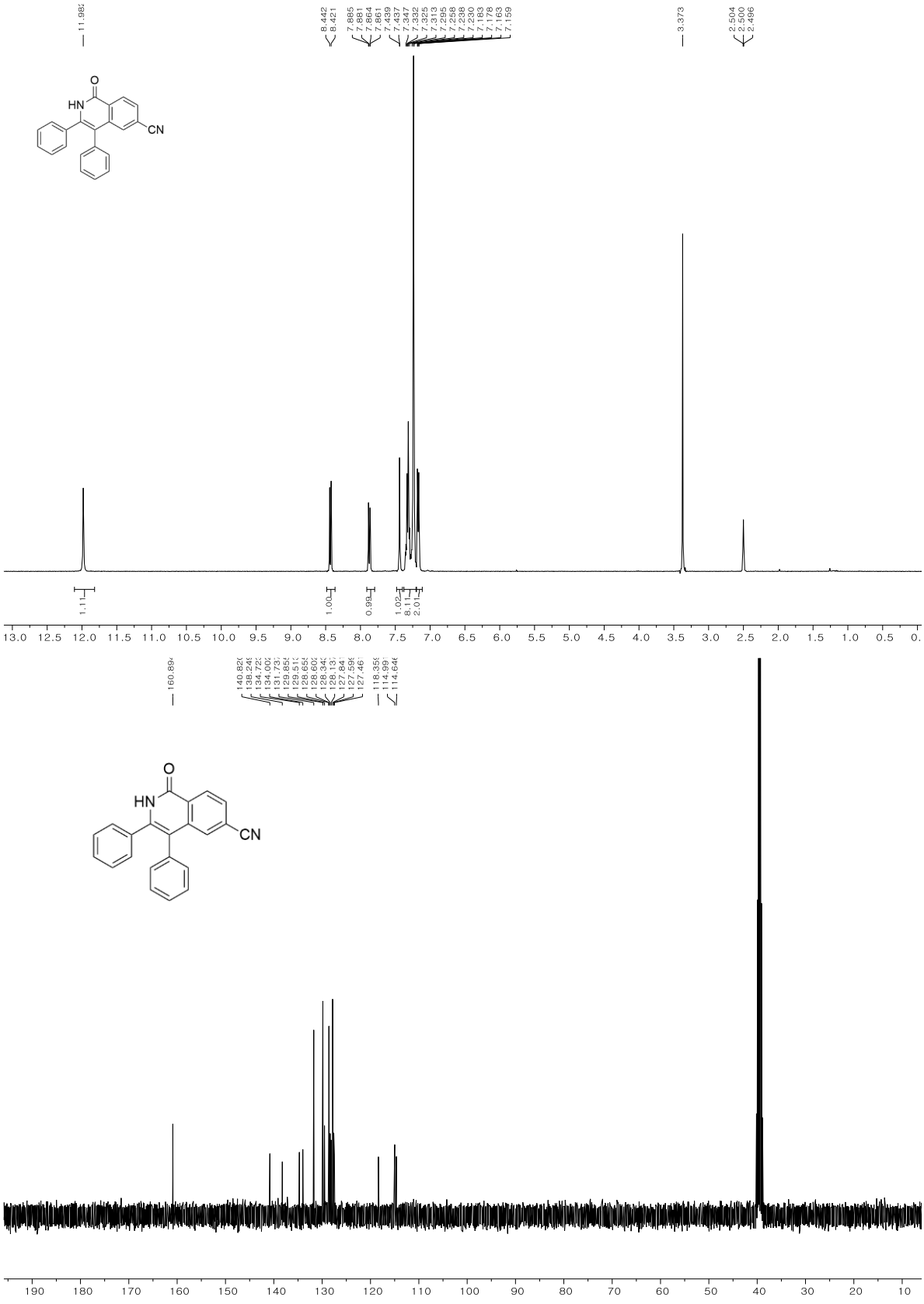
Methyl 1-oxo-3,4-diphenyl-1,2-dihydroisoquinoline-6-carboxylate (10).



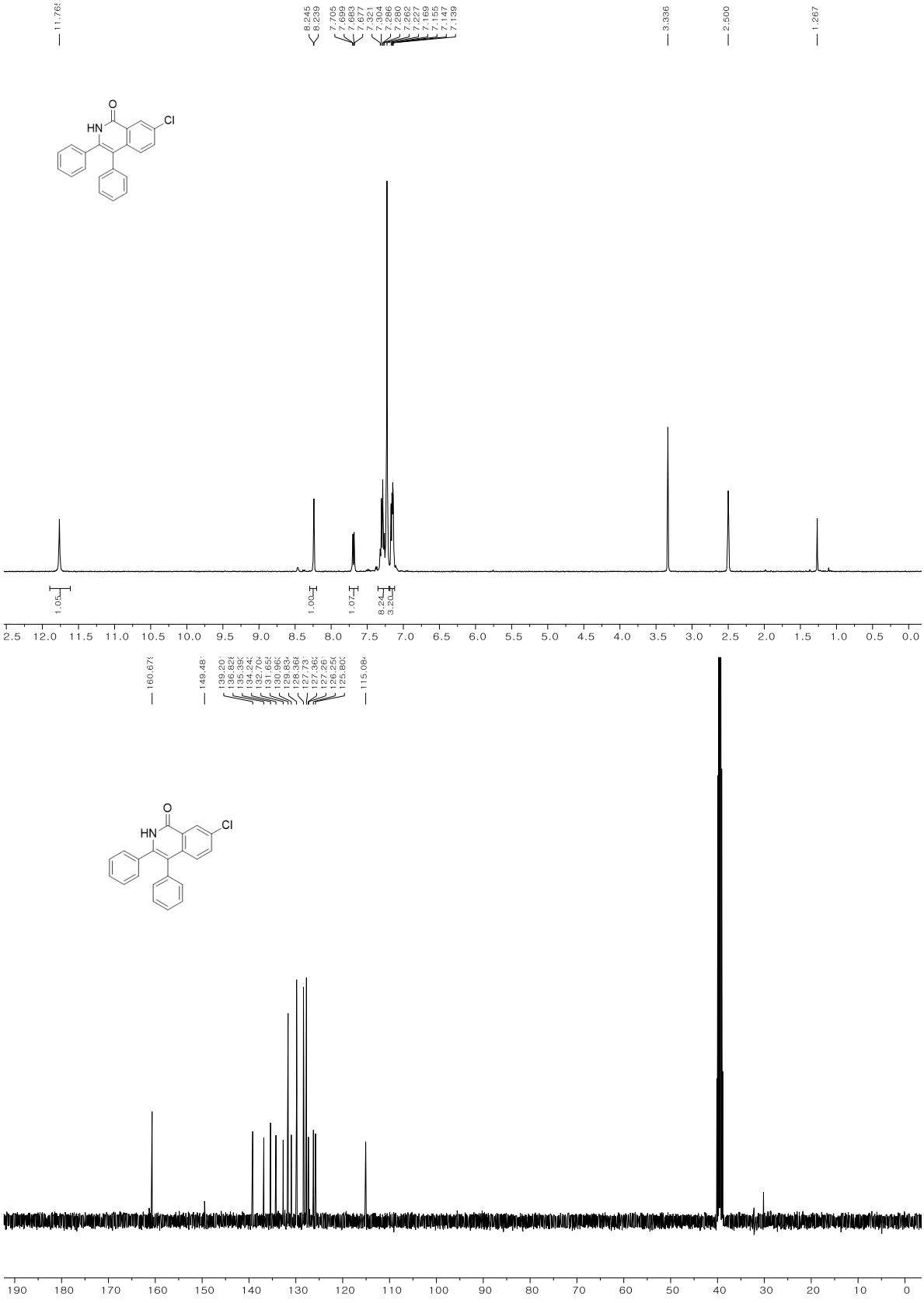
6-(Methylsulfonyl)-3,4-diphenylisoquinolin-1(2H)-one (11).



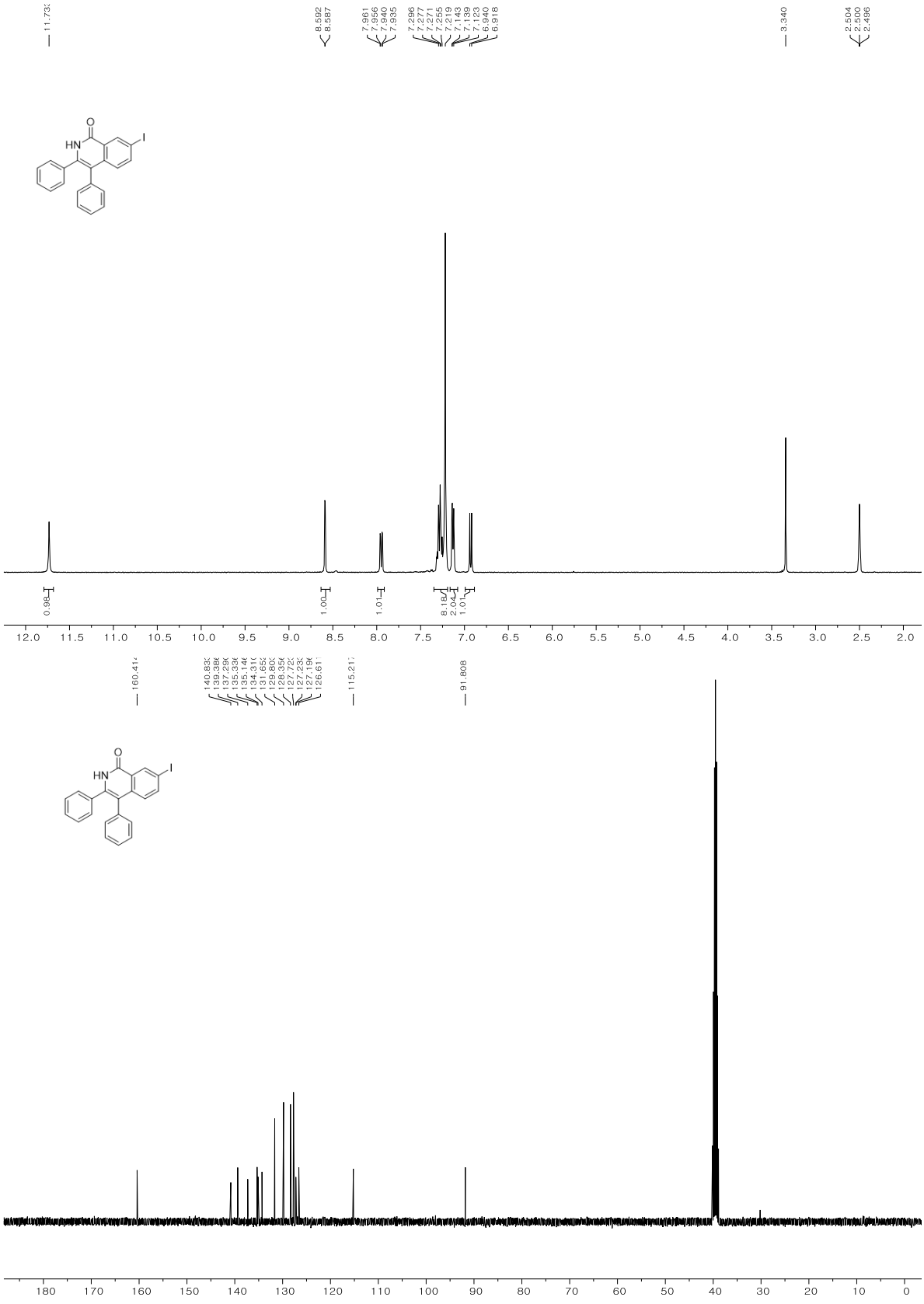
1-Oxo-3,4-diphenyl-1,2-dihydroisoquinoline-6-carbonitrile (12).



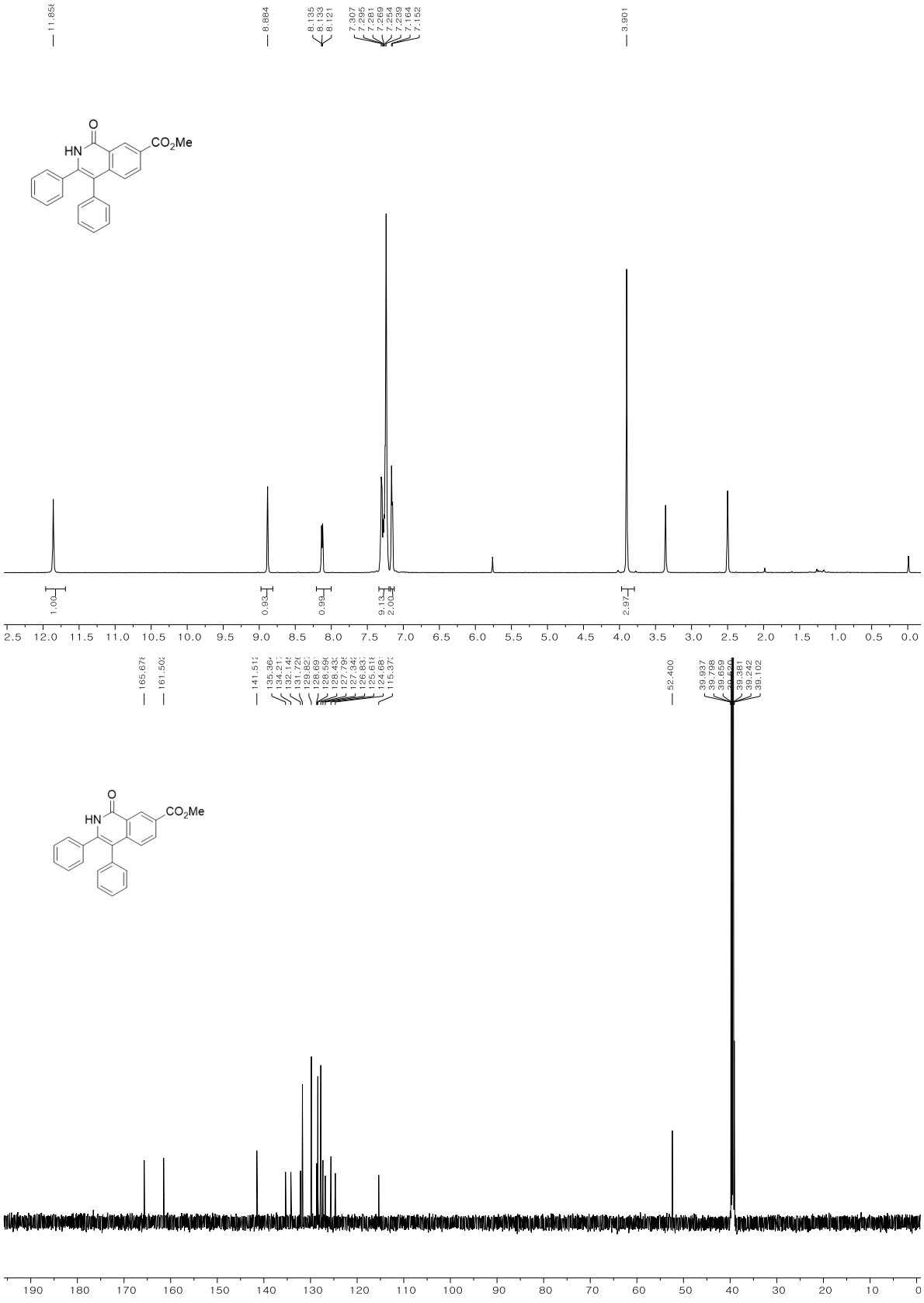
7-Chloro-3,4-diphenylisoquinolin-1(2H)-one (13).



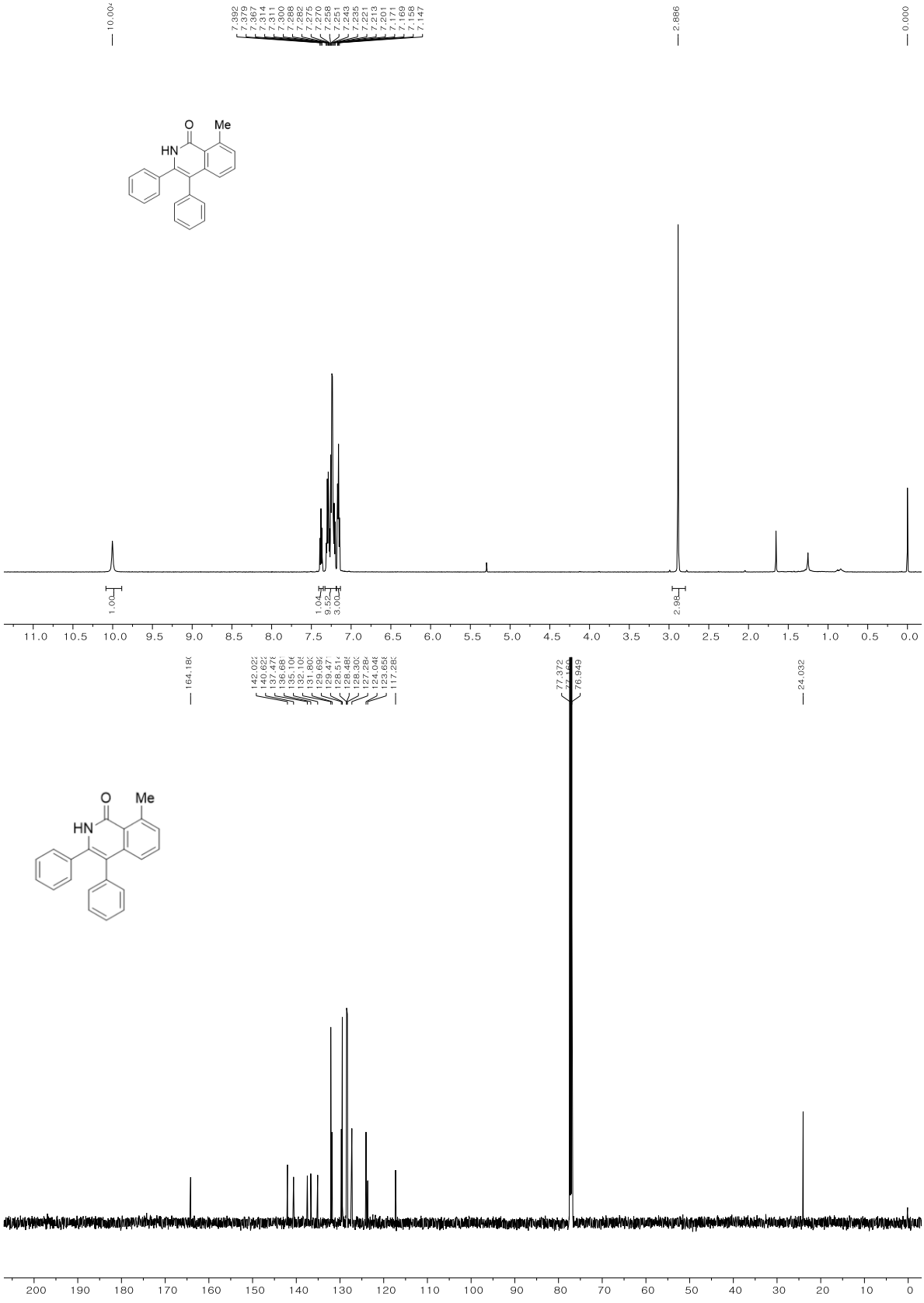
7-Iodo-3,4-diphenylisoquinolin-1(2H)-one (14).



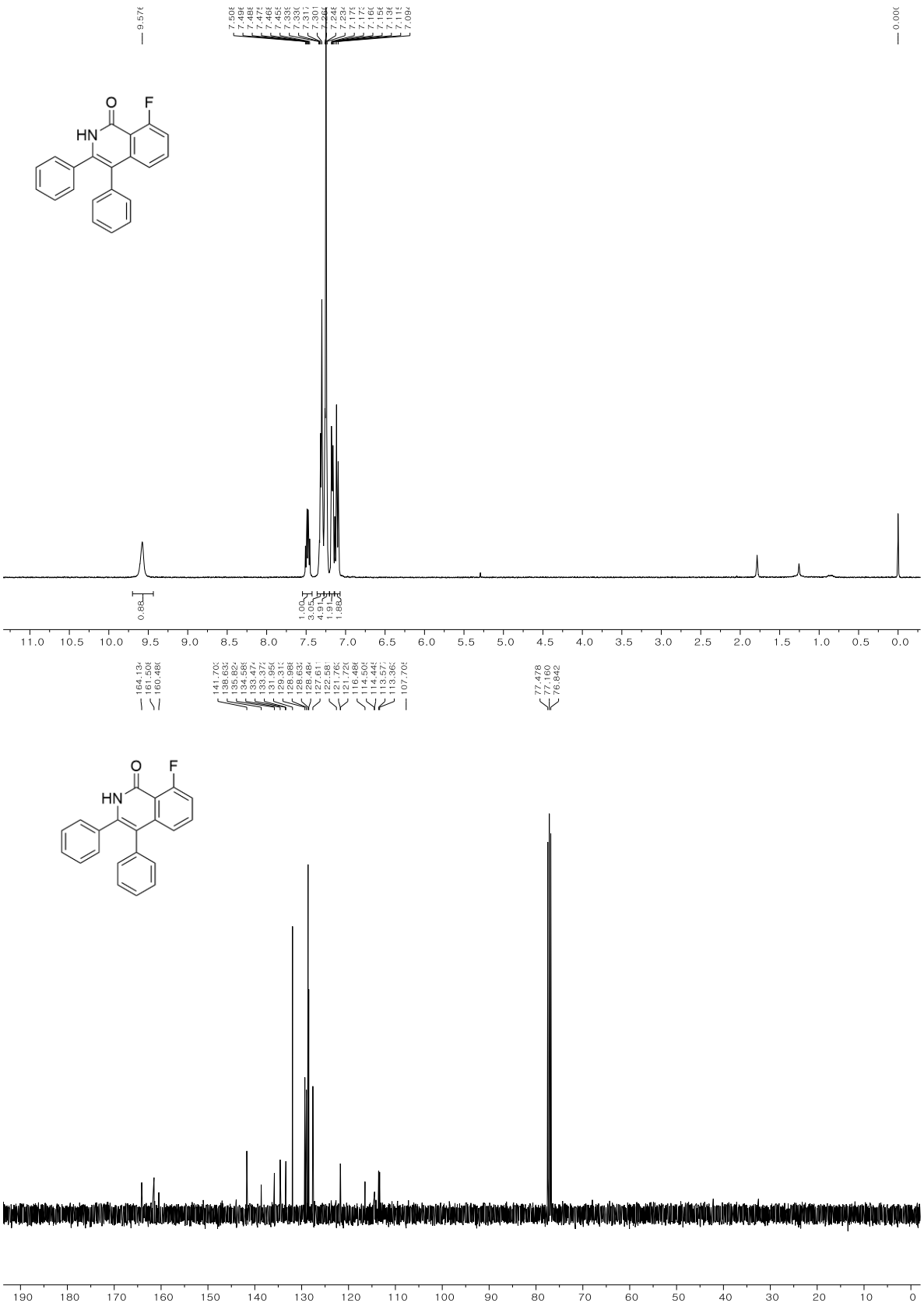
Methyl 1-oxo-3,4-diphenyl-1,2-dihydroisoquinoline-7-carboxylate (15).



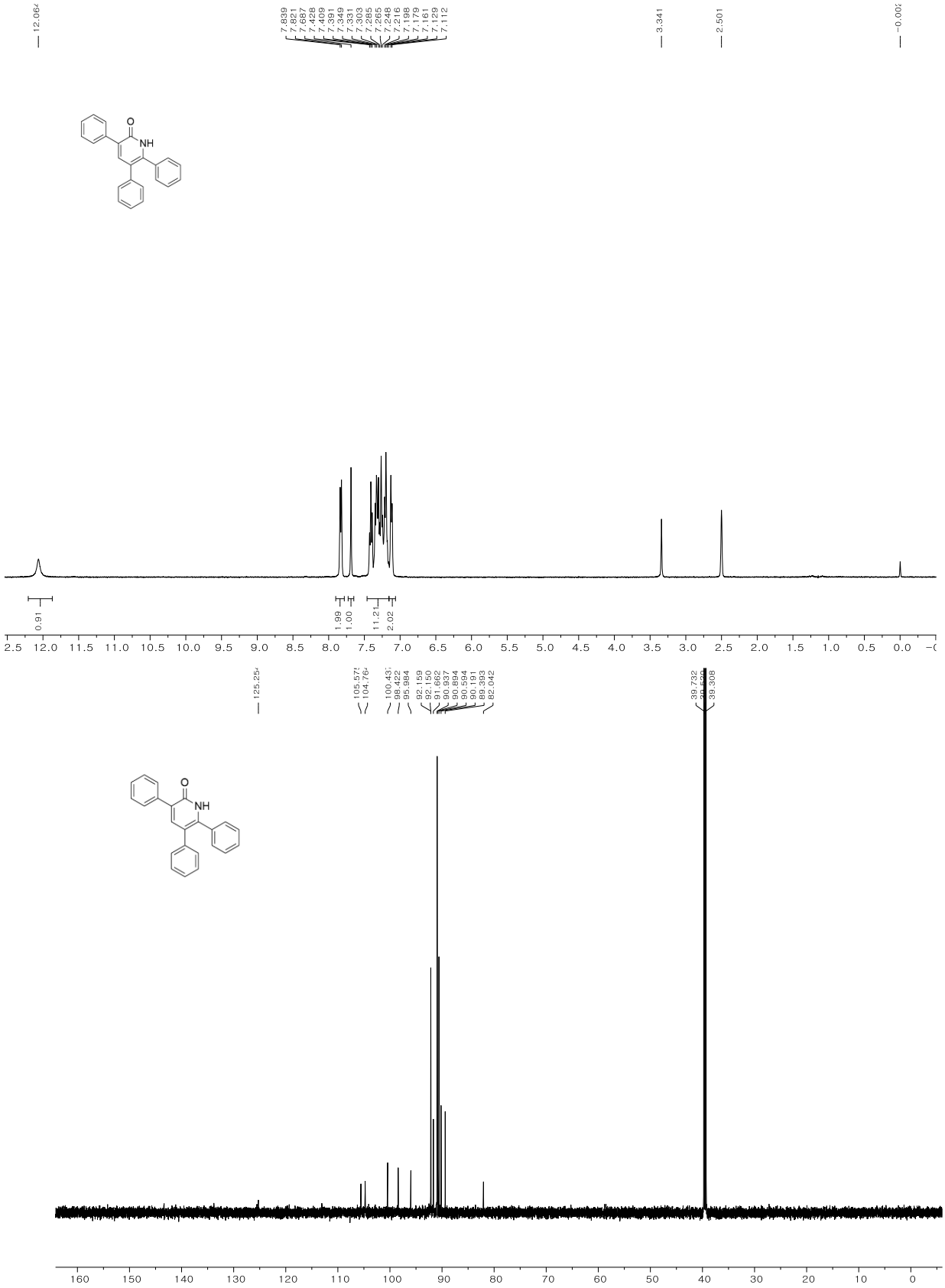
8-Methyl-3,4-diphenylisoquinolin-1(2H)-one (16).



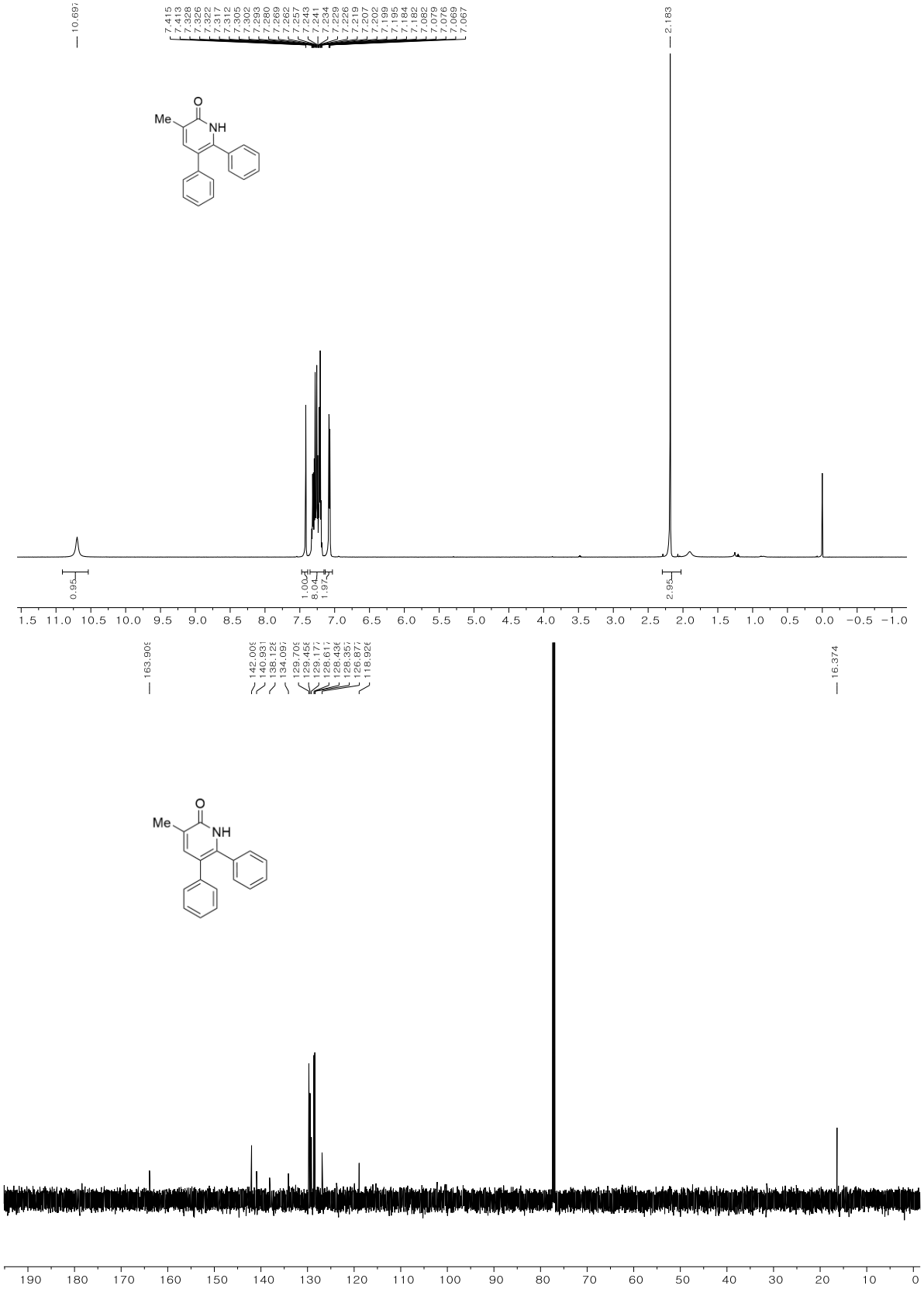
8-Fluoro-3,4-diphenylisoquinolin-1(2H)-one (17).



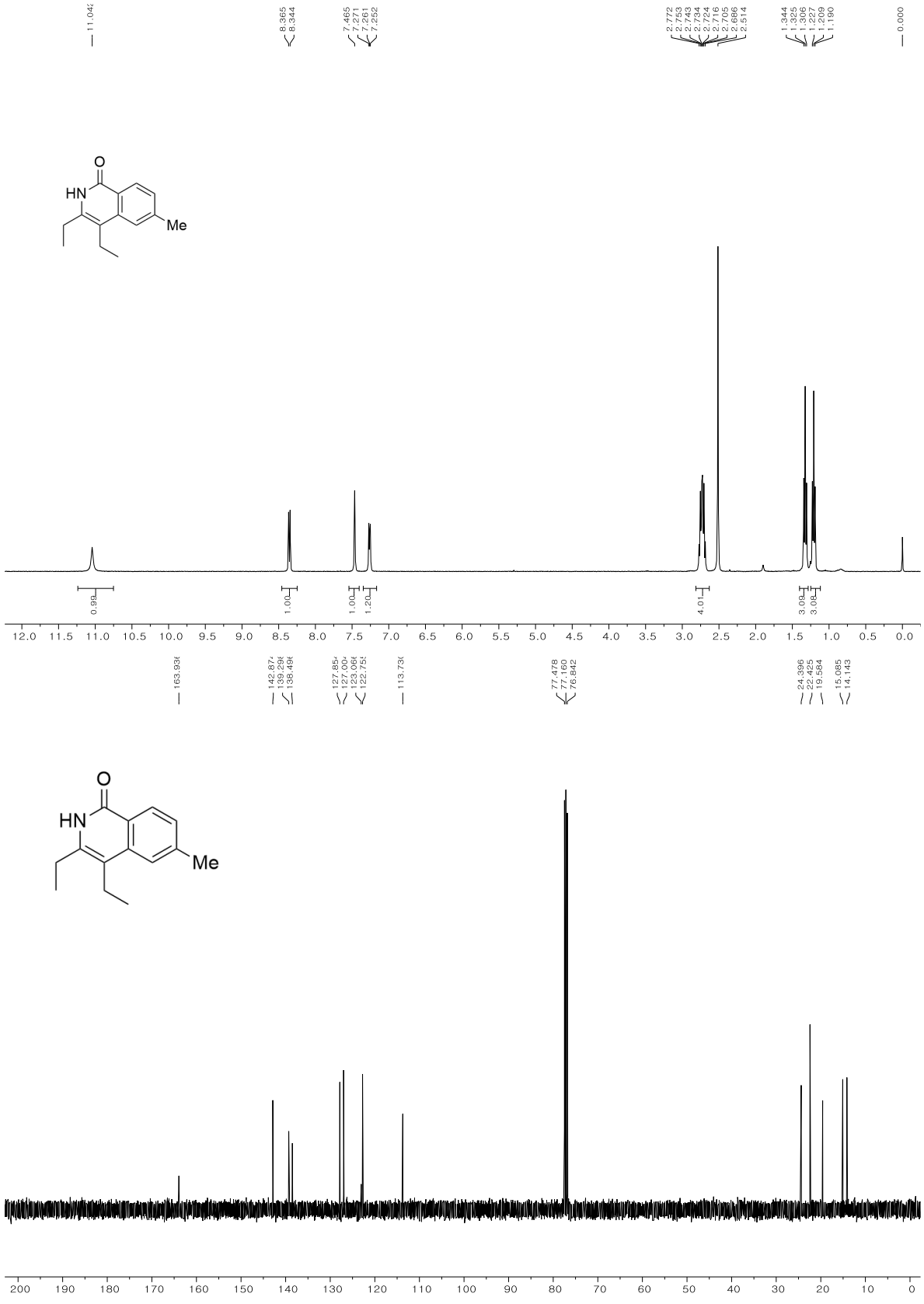
3,5,6-Triphenylpyridin-2(1H)-one (18).



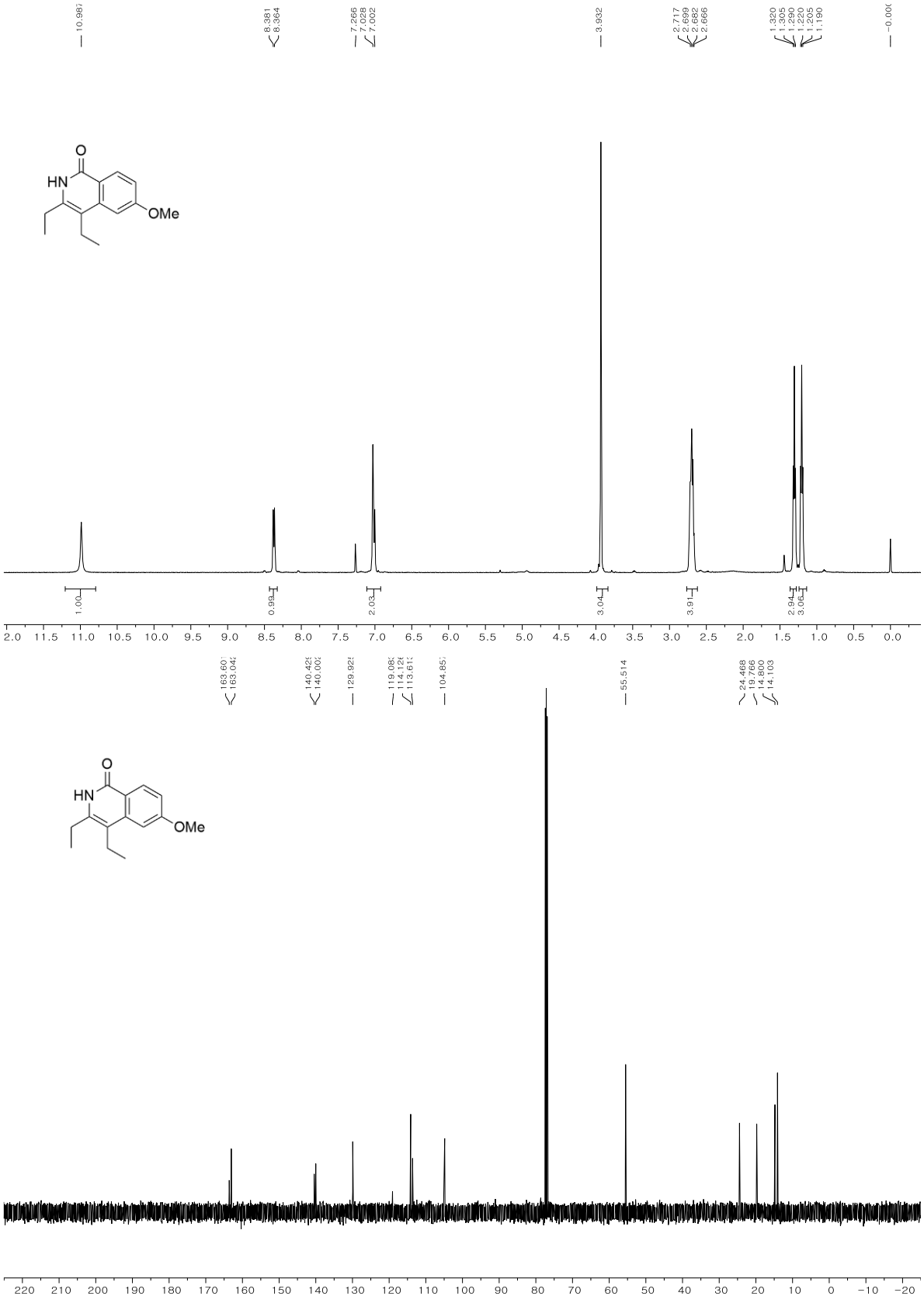
3,5,6-Triphenylpyridin-2(1H)-one (19).



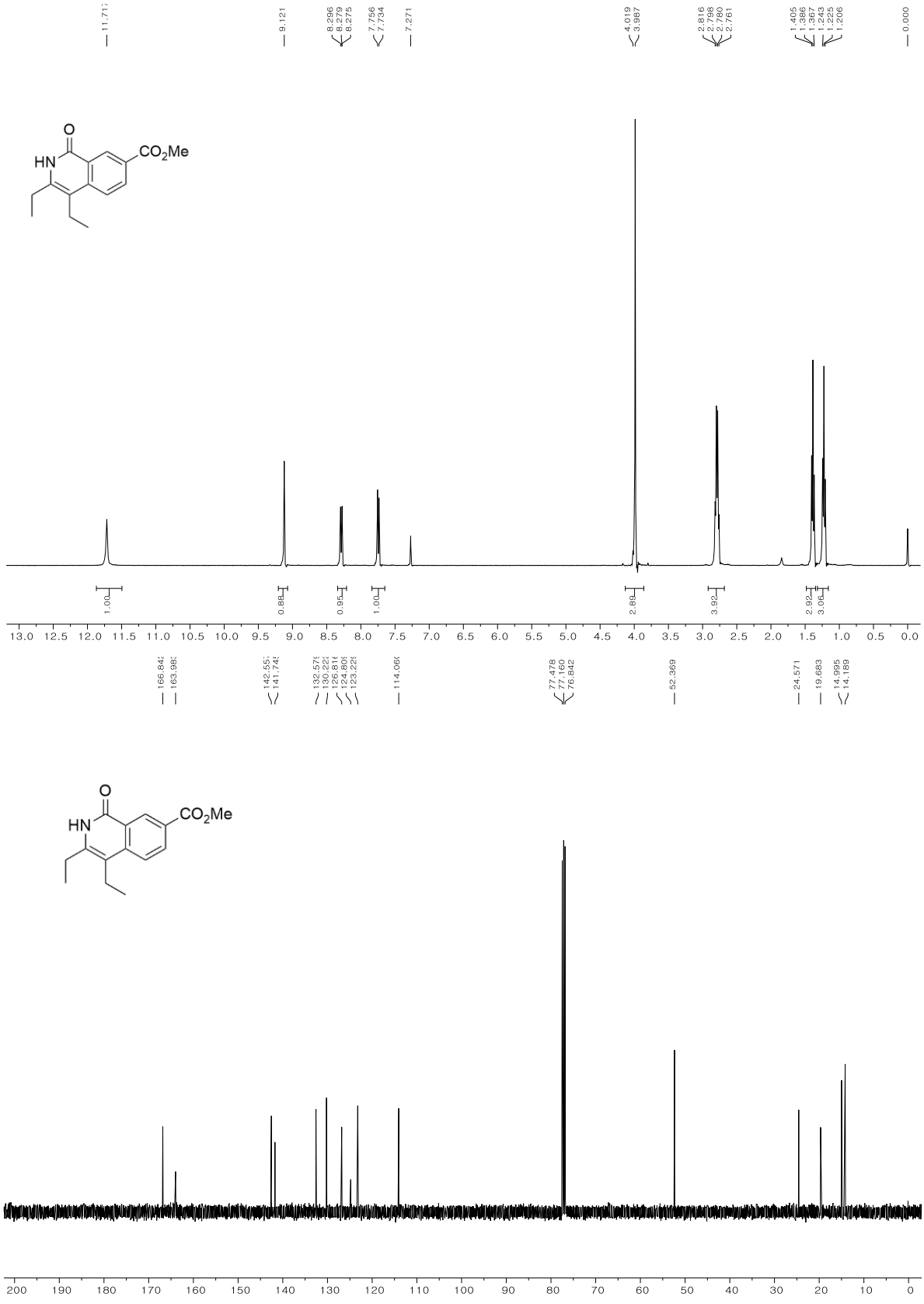
3,4-Diethyl-6-methylisoquinolin-1(2H)-one (20).



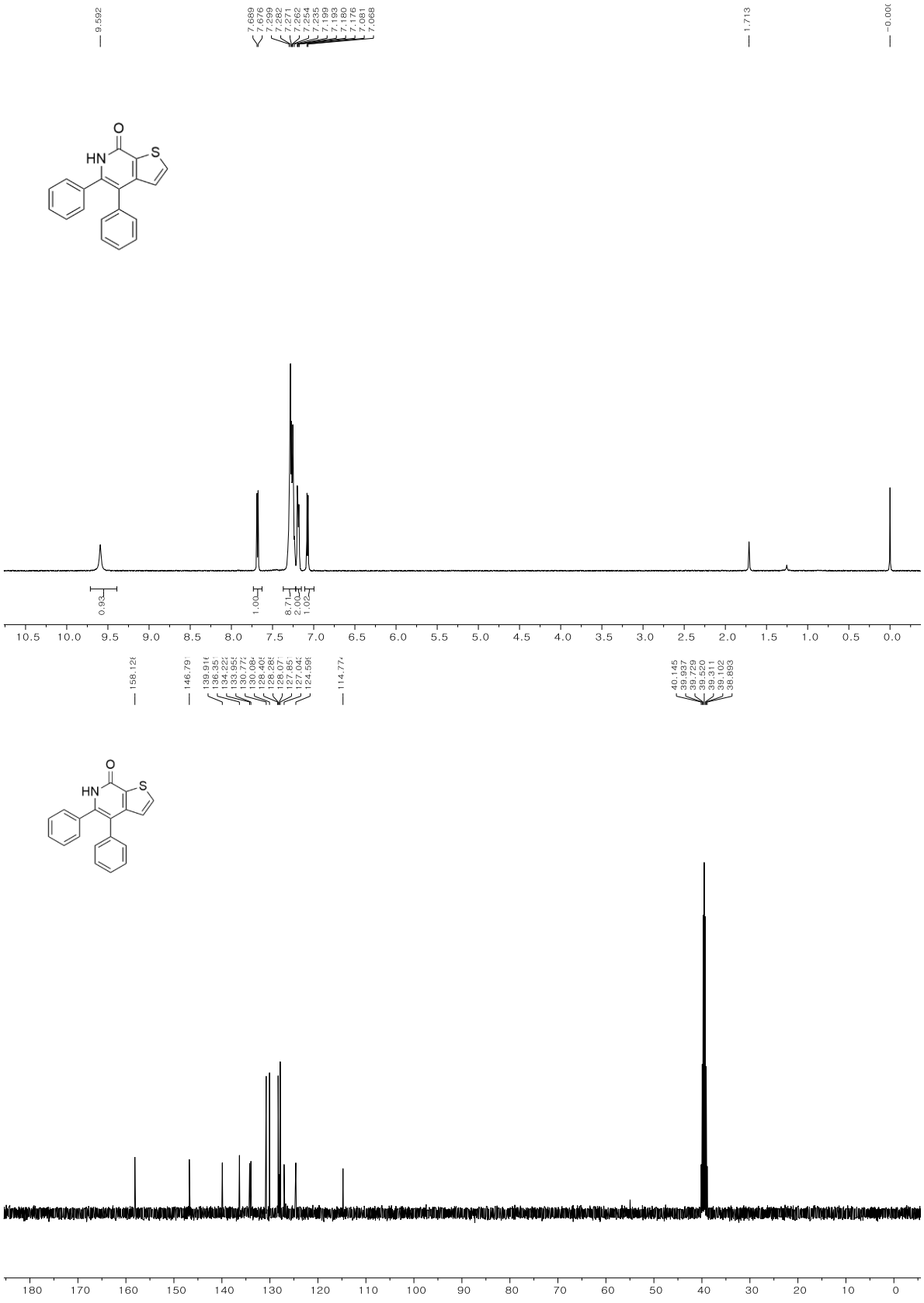
3,4-Diethyl-6-methoxyisoquinolin-1(2H)-one (21).



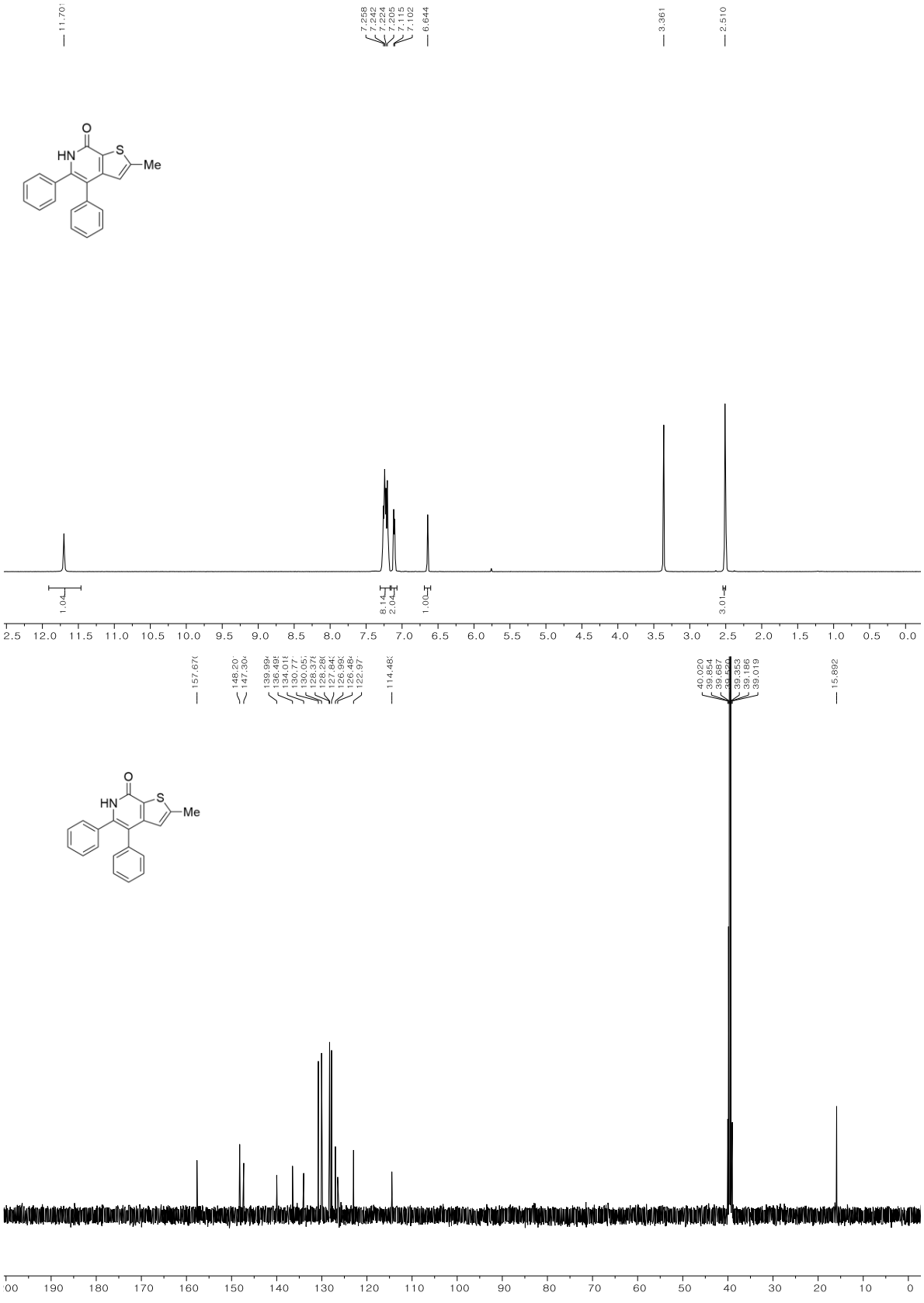
Methyl 3,4-diethyl-1-oxo-1,2-dihydroisoquinoline-7-carboxylate (22).



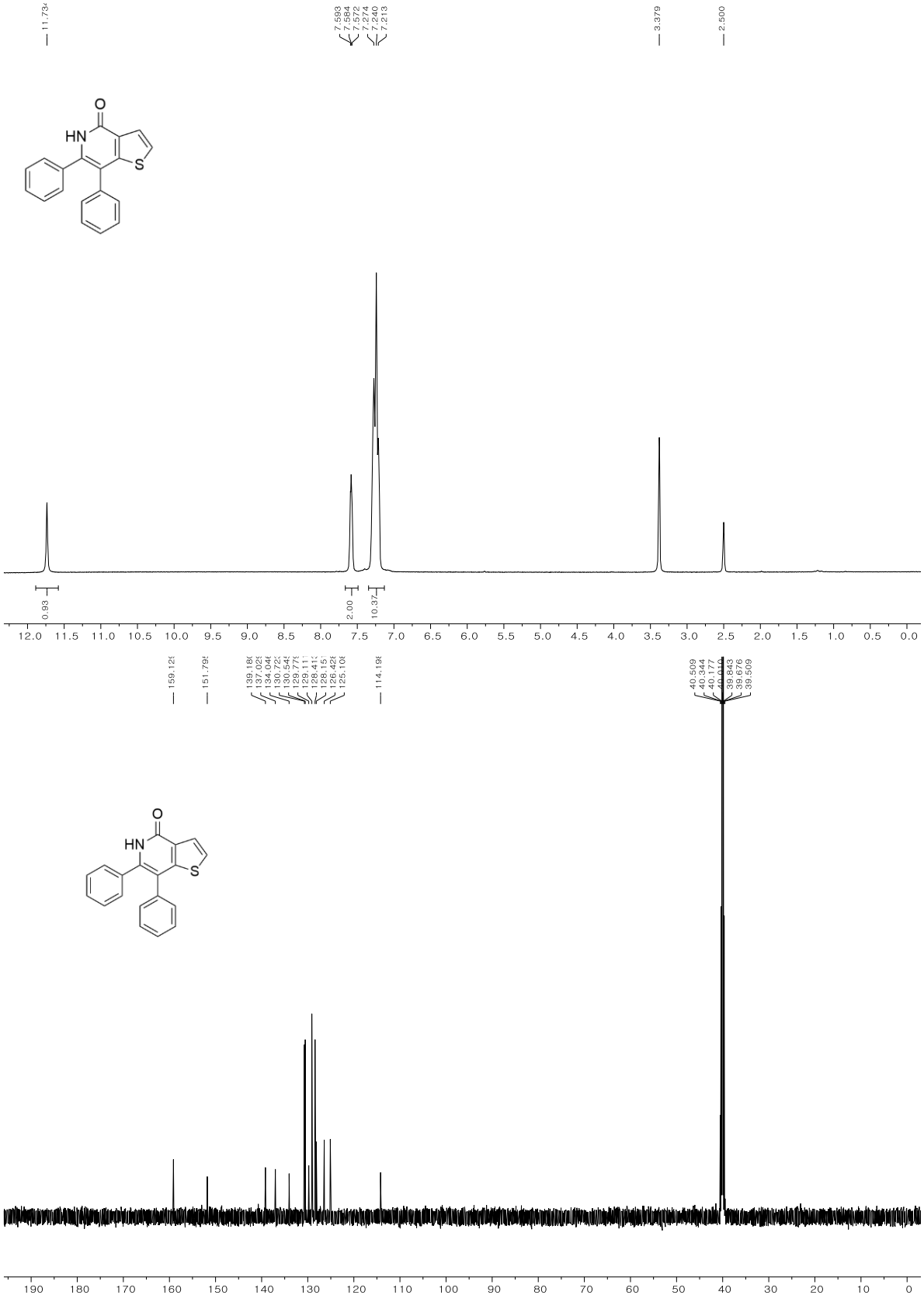
4,5-Diphenylthieno[2,3-c]pyridin-7(6H)-one (23).



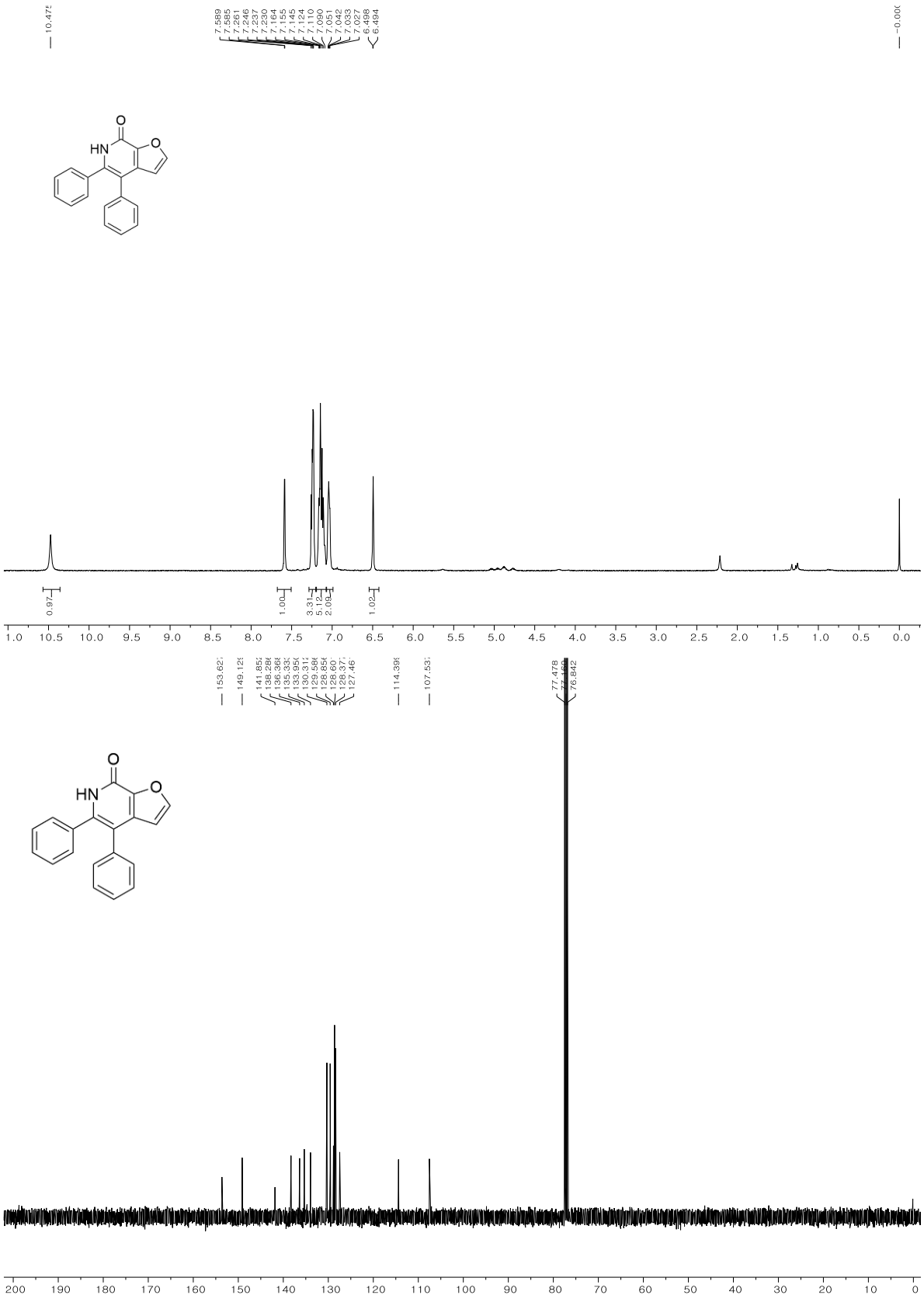
2-Methyl-4,5-diphenylthieno[2,3-c]pyridin-7(6H)-one (24).



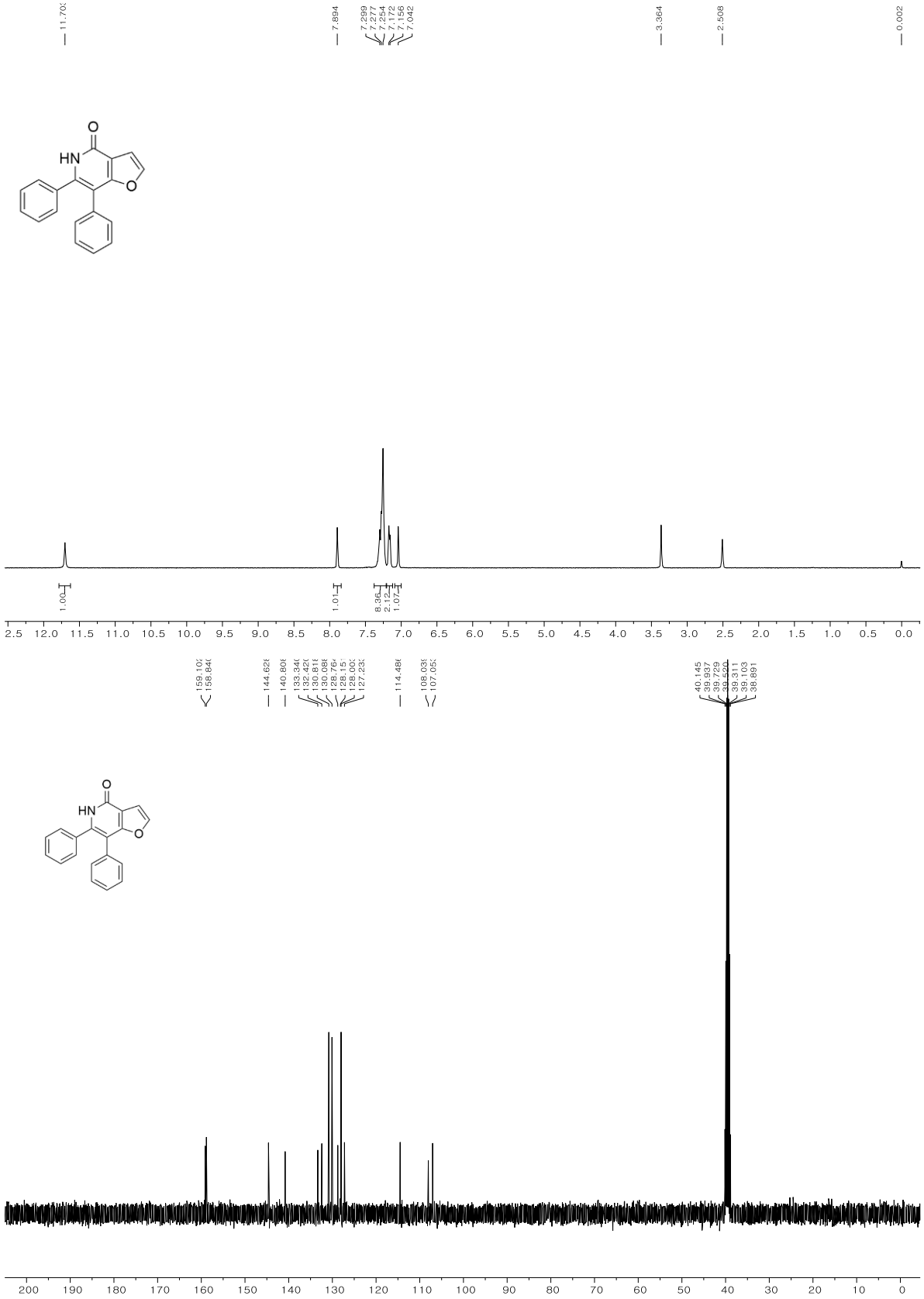
6,7-Diphenylthieno[3,2-c]pyridin-4(5H)-one (25).



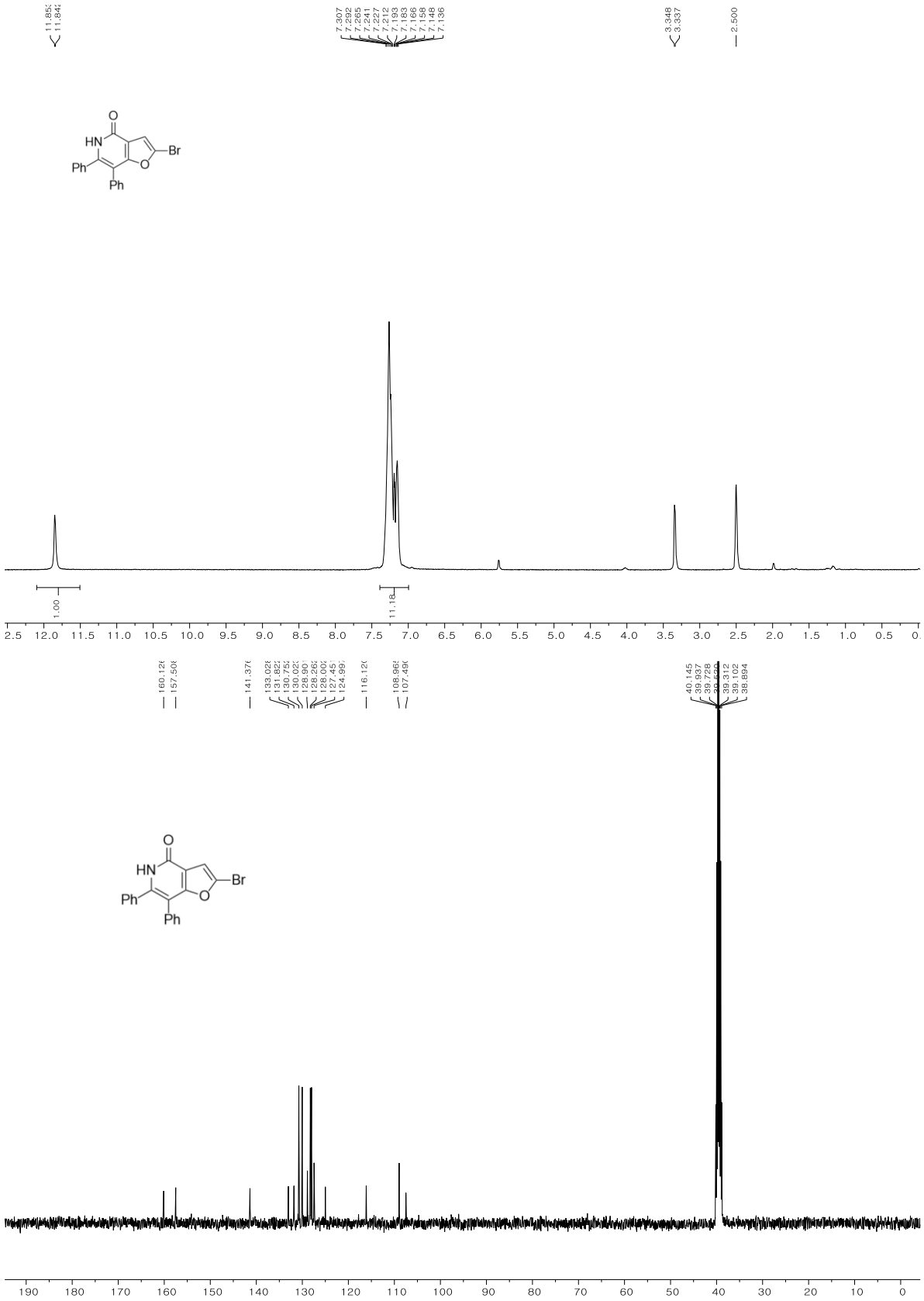
4,5-Diphenylfuro[2,3-c]pyridin-7(6H)-one (26).



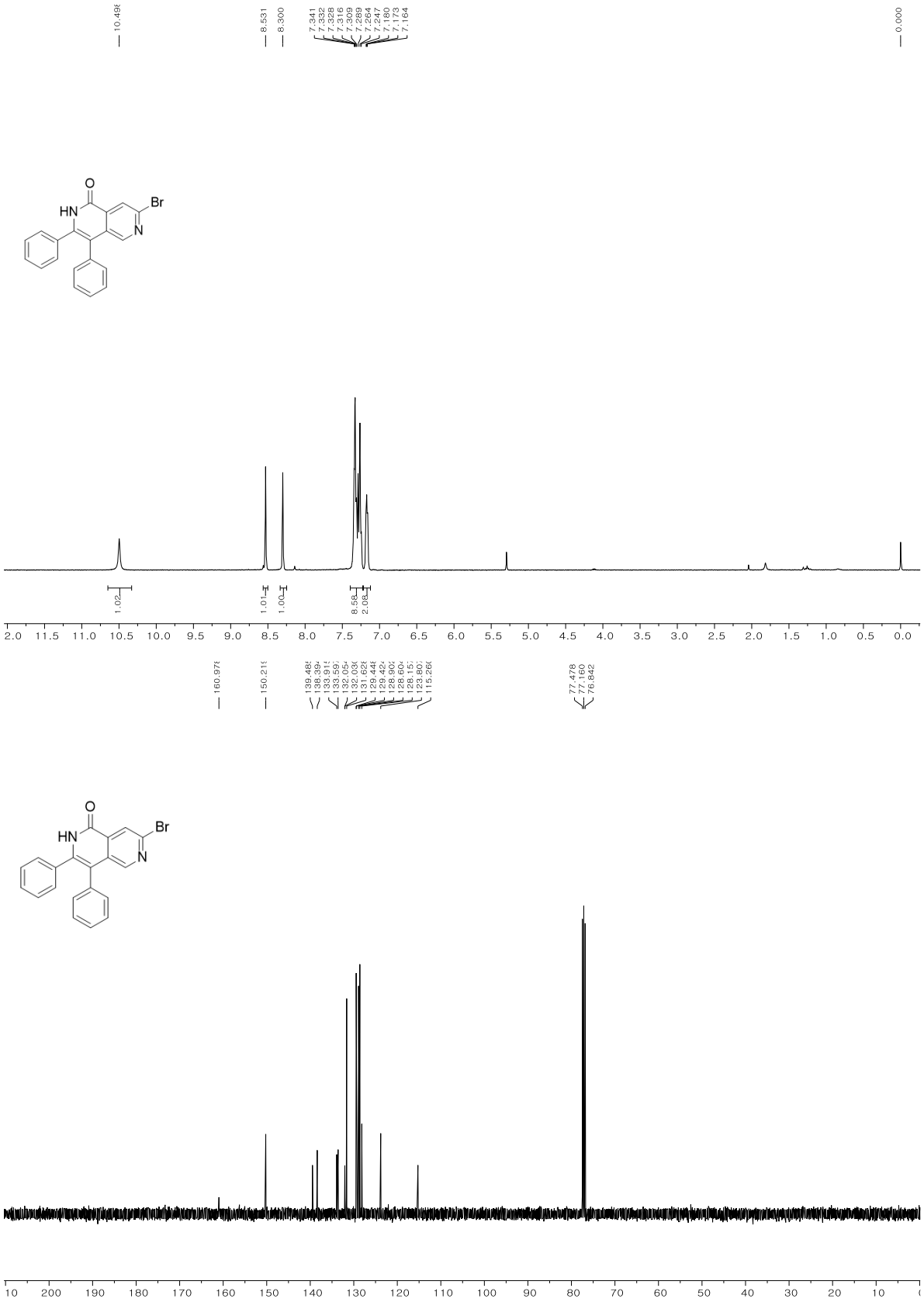
6,7-Diphenylfuro[3,2-c]pyridin-4(5H)-one (27).



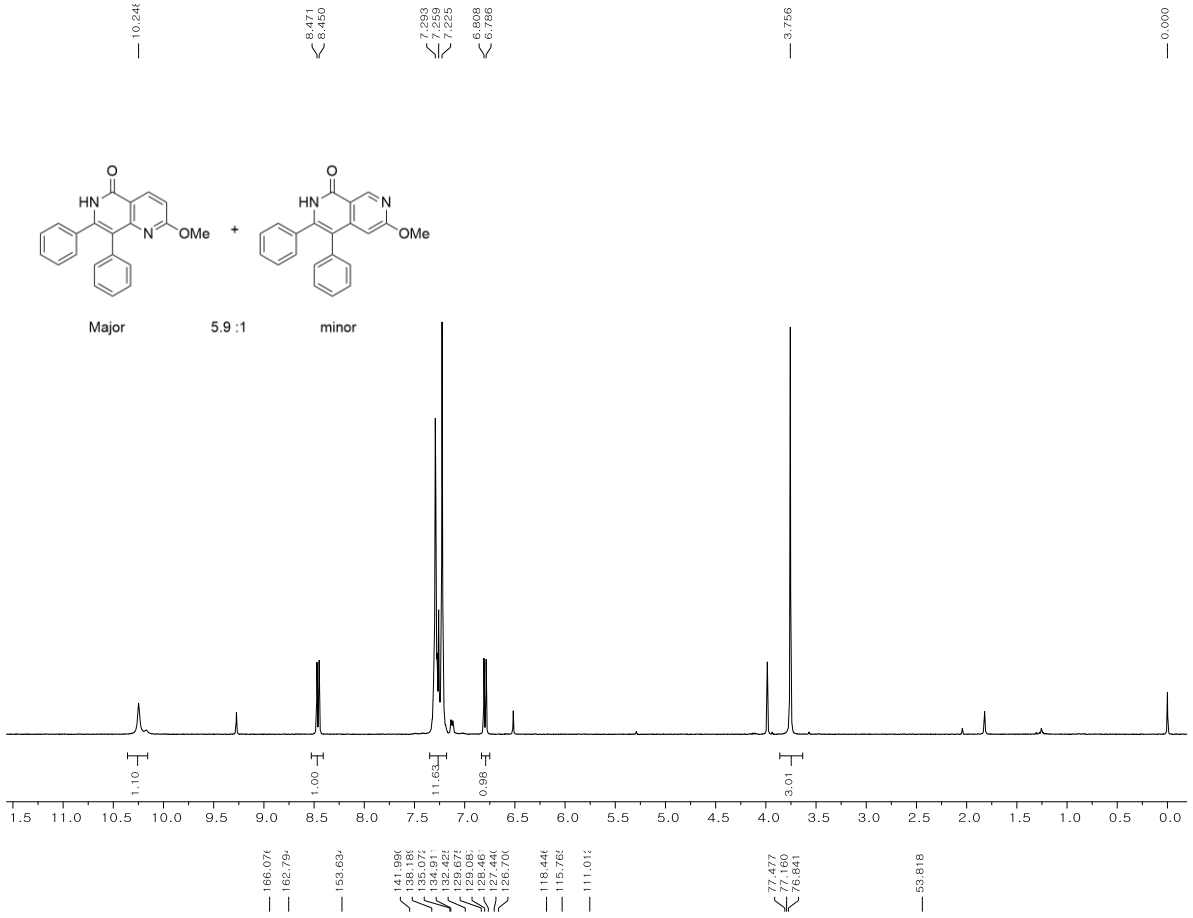
2-Bromo-6,7-diphenylfuro[3,2-c]pyridin-4(5H)-one (28).

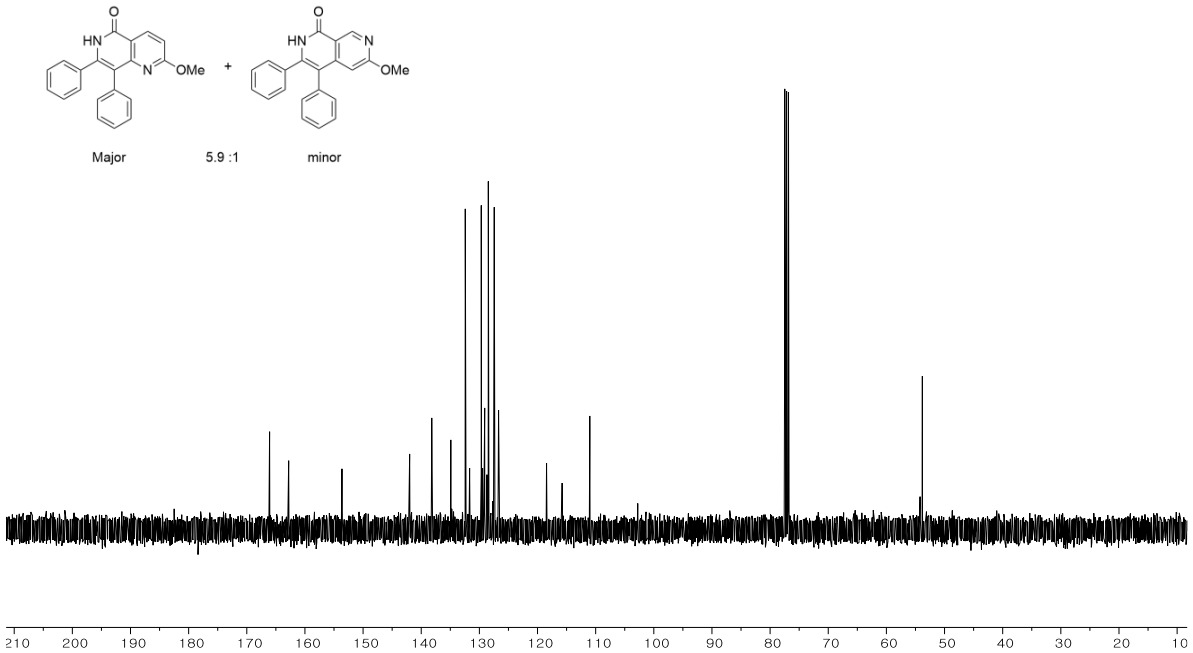


7-Bromo-3,4-diphenyl-2,6-naphthyridin-1(2H)-one (29).

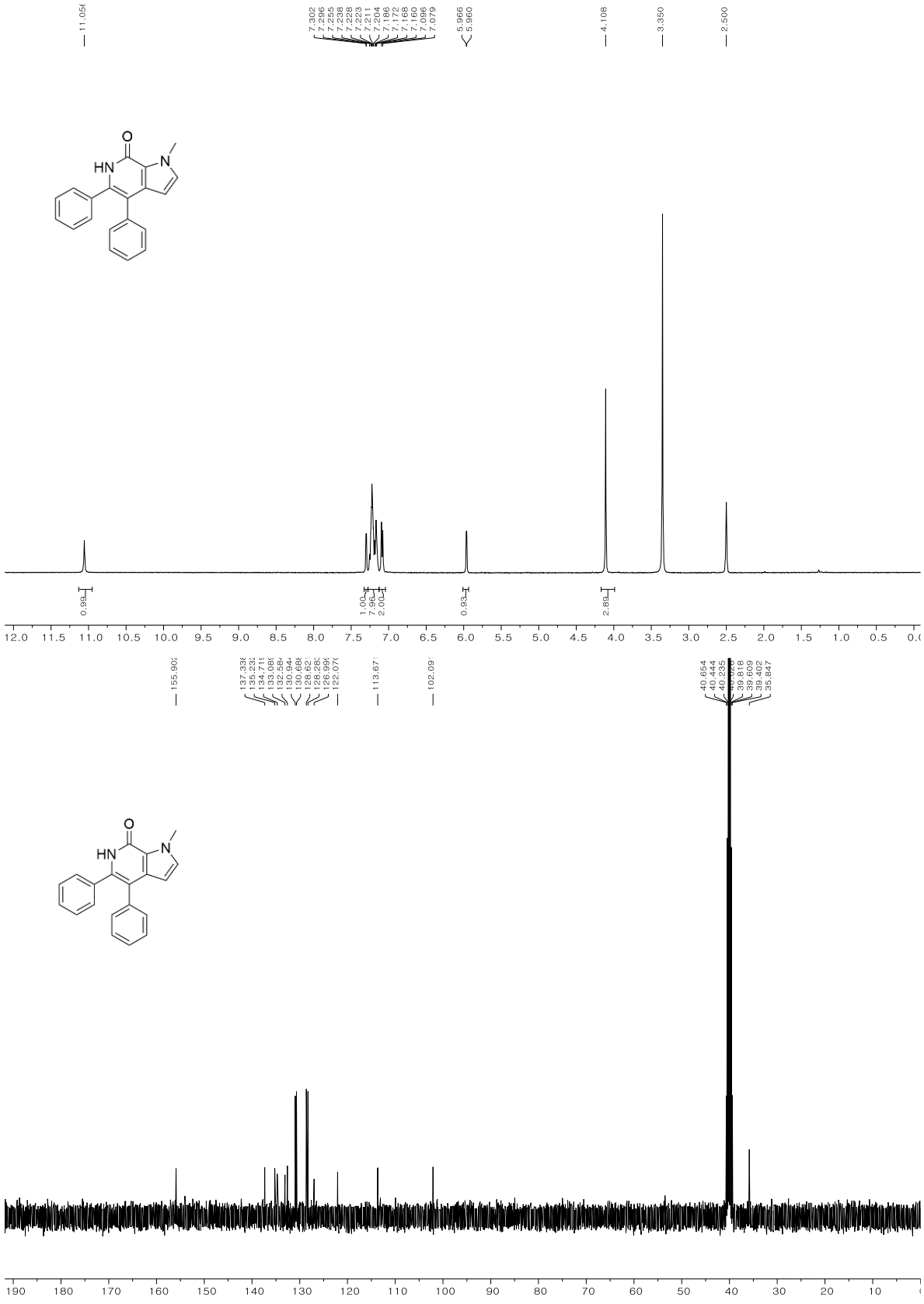


2-Methoxy-7,8-diphenyl-1,6-naphthyridin-5(6H)-one (30).

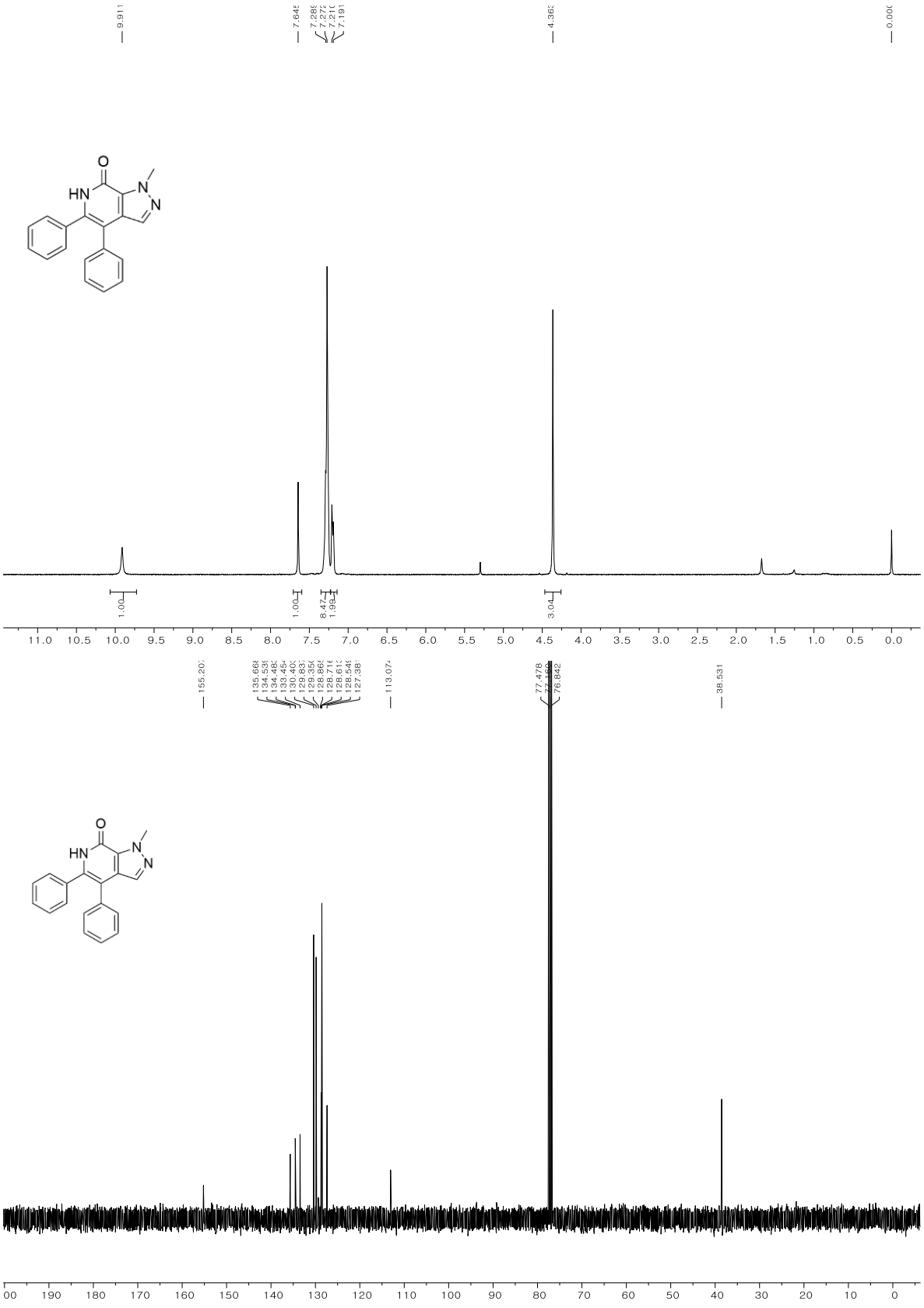




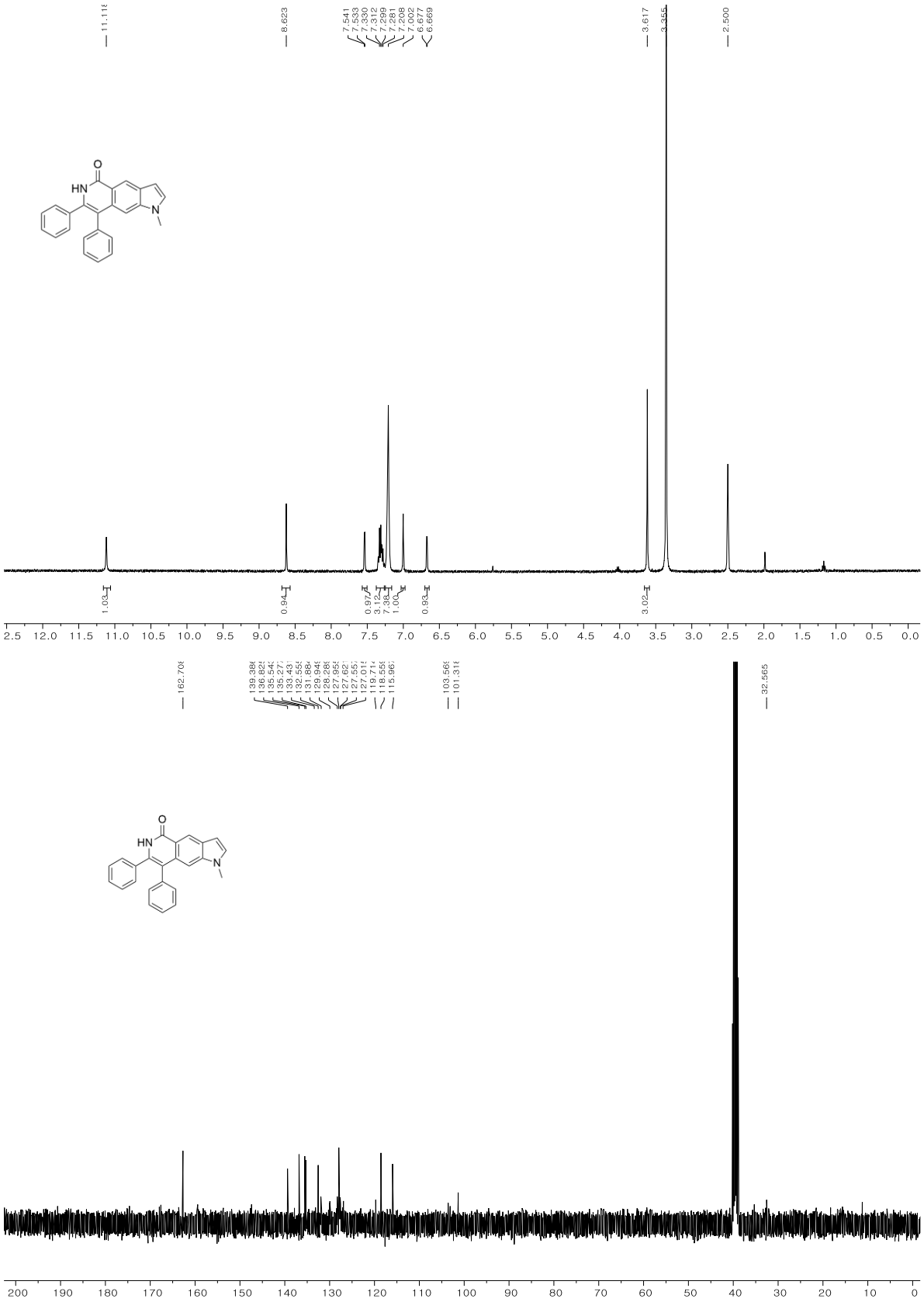
1-Methyl-4,5-diphenyl-1,6-dihydro-7H-pyrrolo[2,3-c]pyridin-7-one (31).



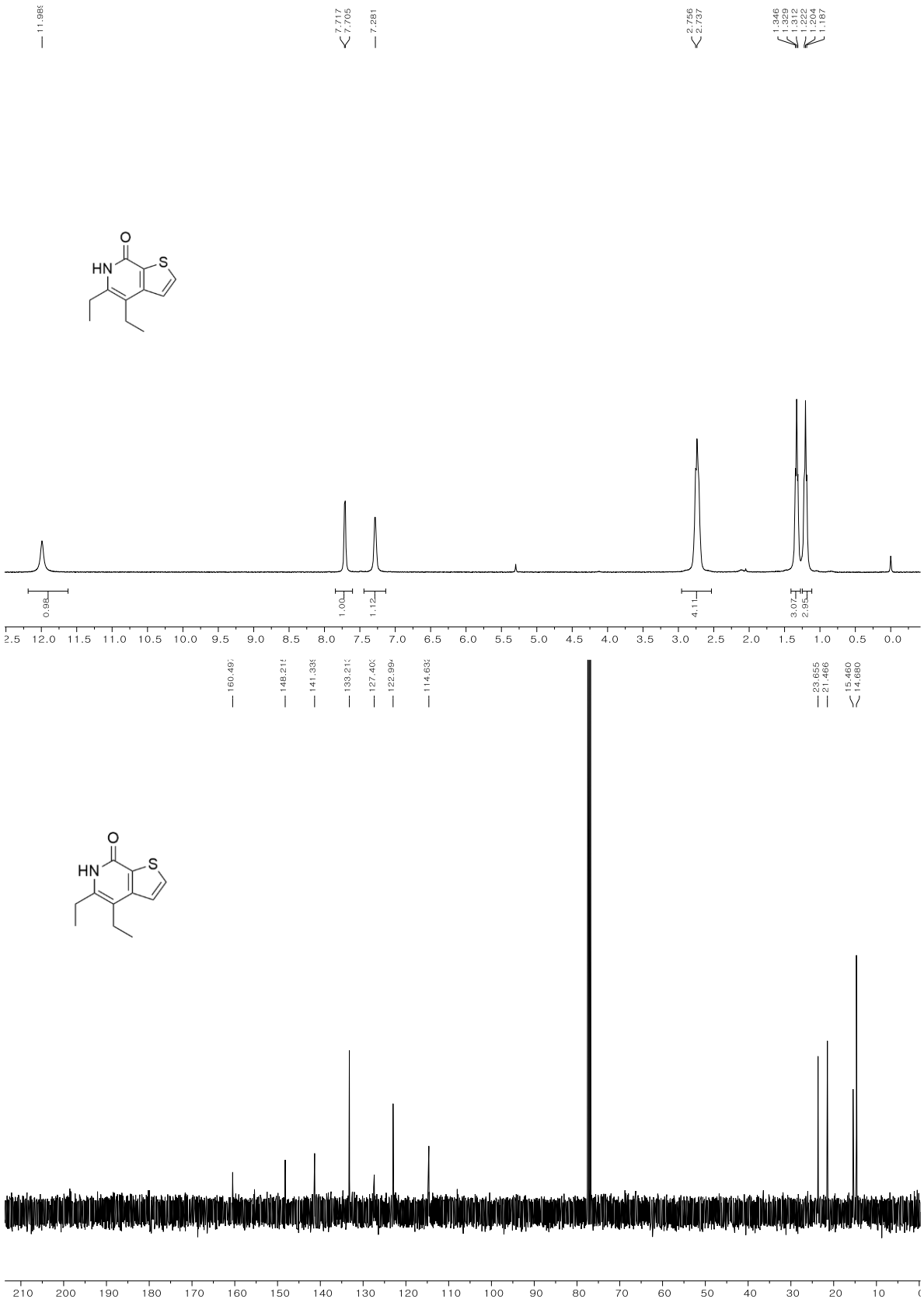
1-Methyl-4,5-diphenyl-1,6-dihydro-7H-pyrazolo[3,4-c]pyridin-7-one (32).



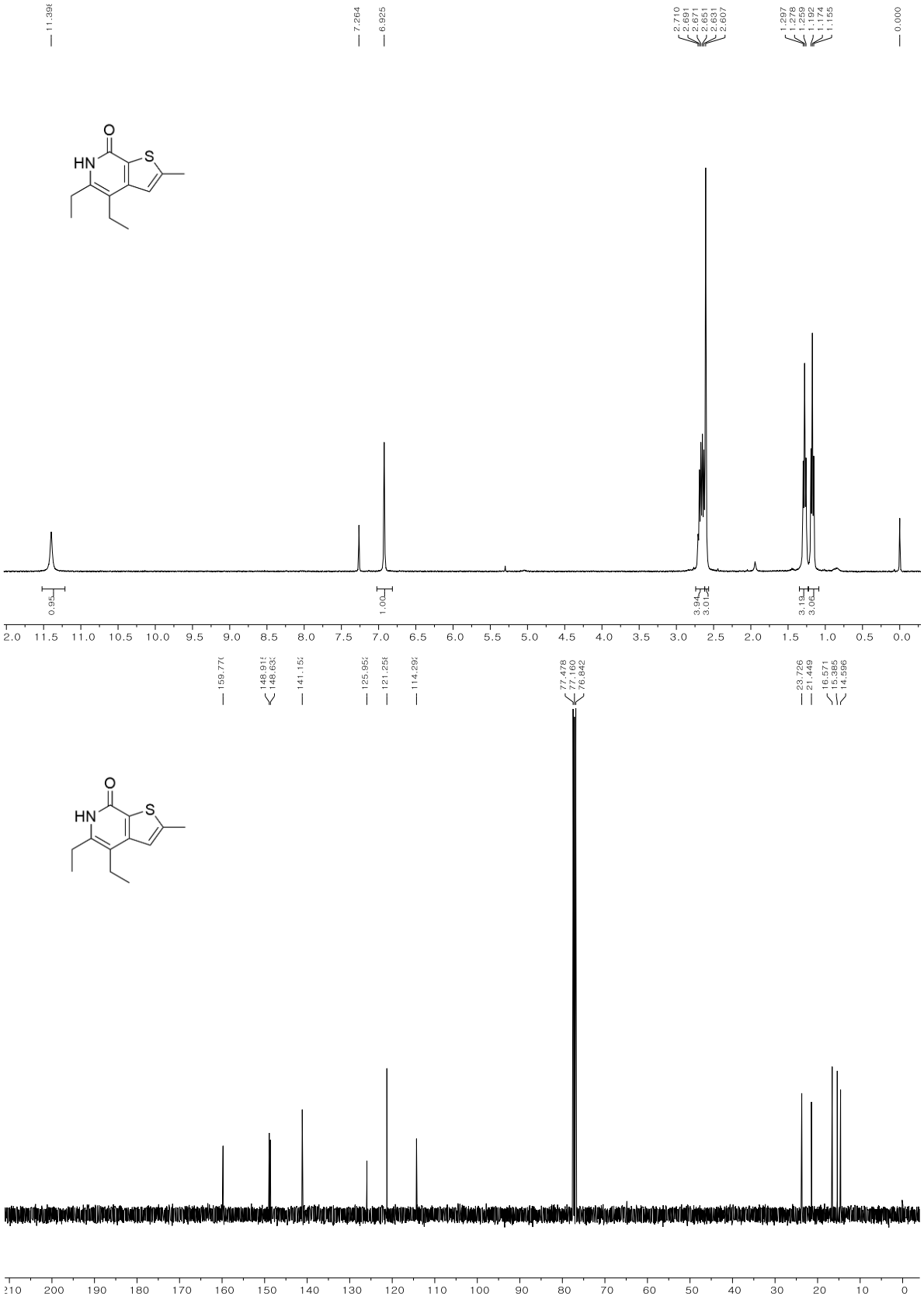
z1-Methyl-7,8-diphenyl-1,6-dihydro-5H-pyrrolo[2,3-g]isoquinolin-5-one (33).



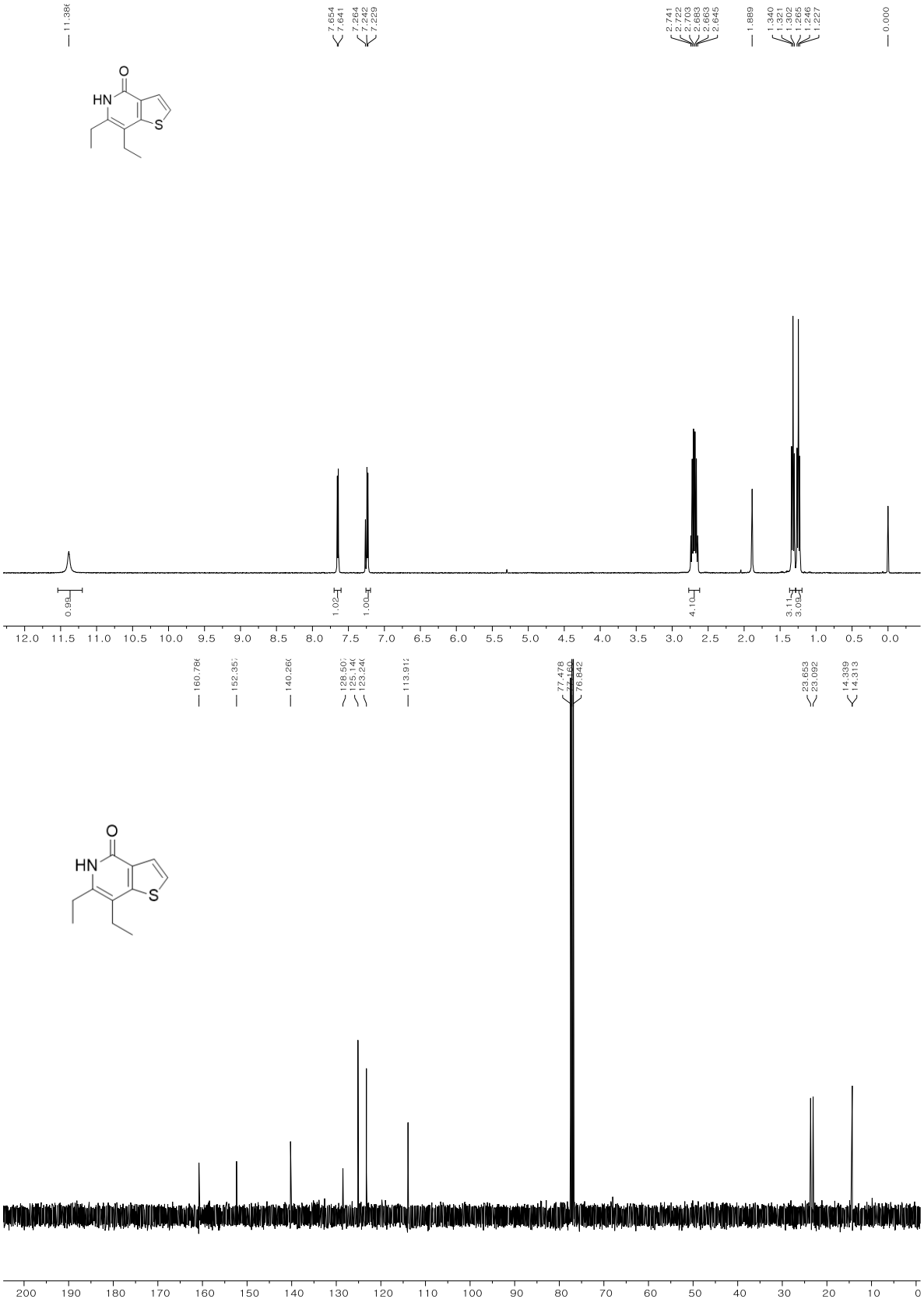
4,5-Diethylthieno[2,3-c]pyridin-7(6H)-one (34).



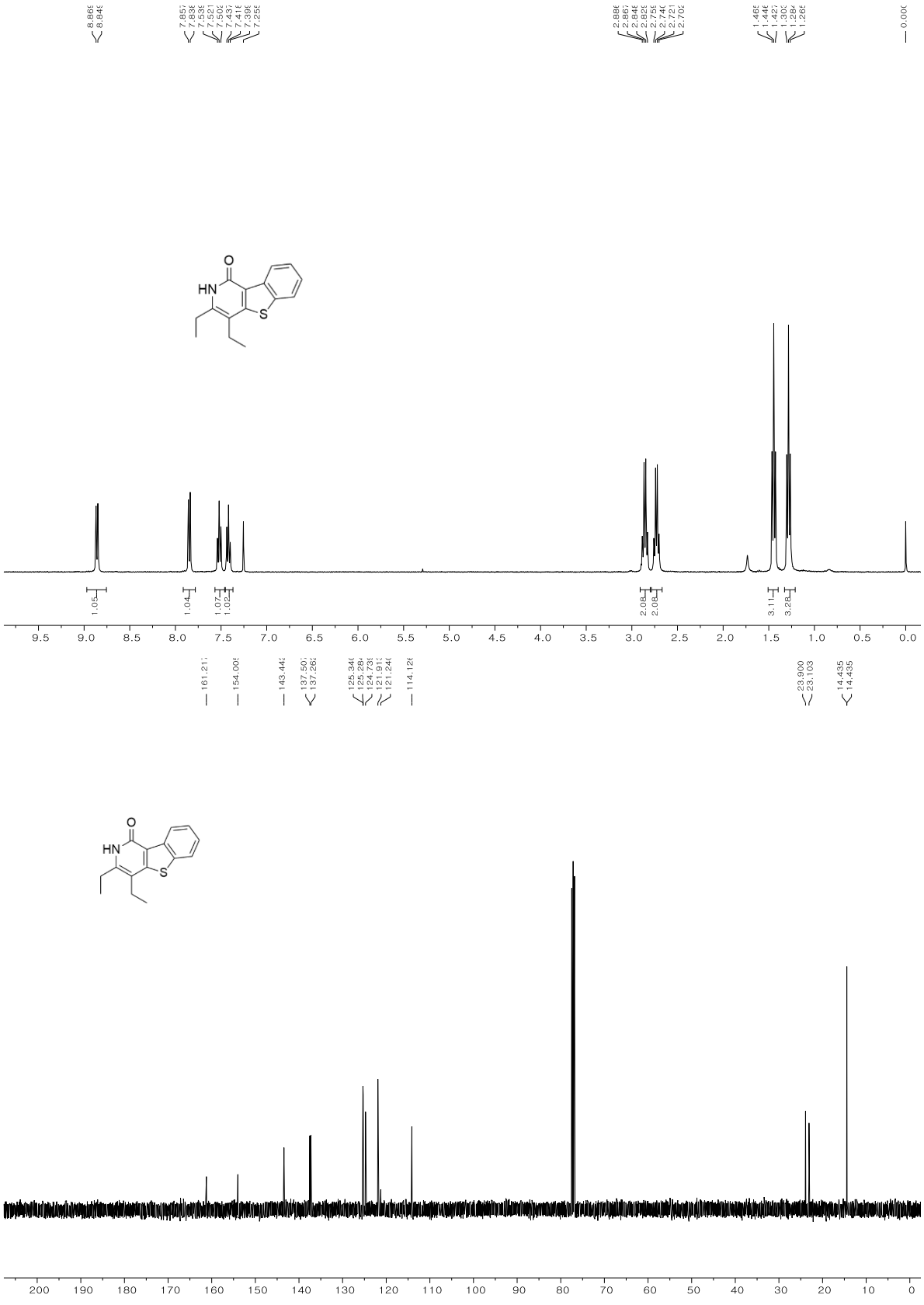
4,5-Diethyl-2-methylthieno[2,3-c]pyridin-7(6H)-one (35).



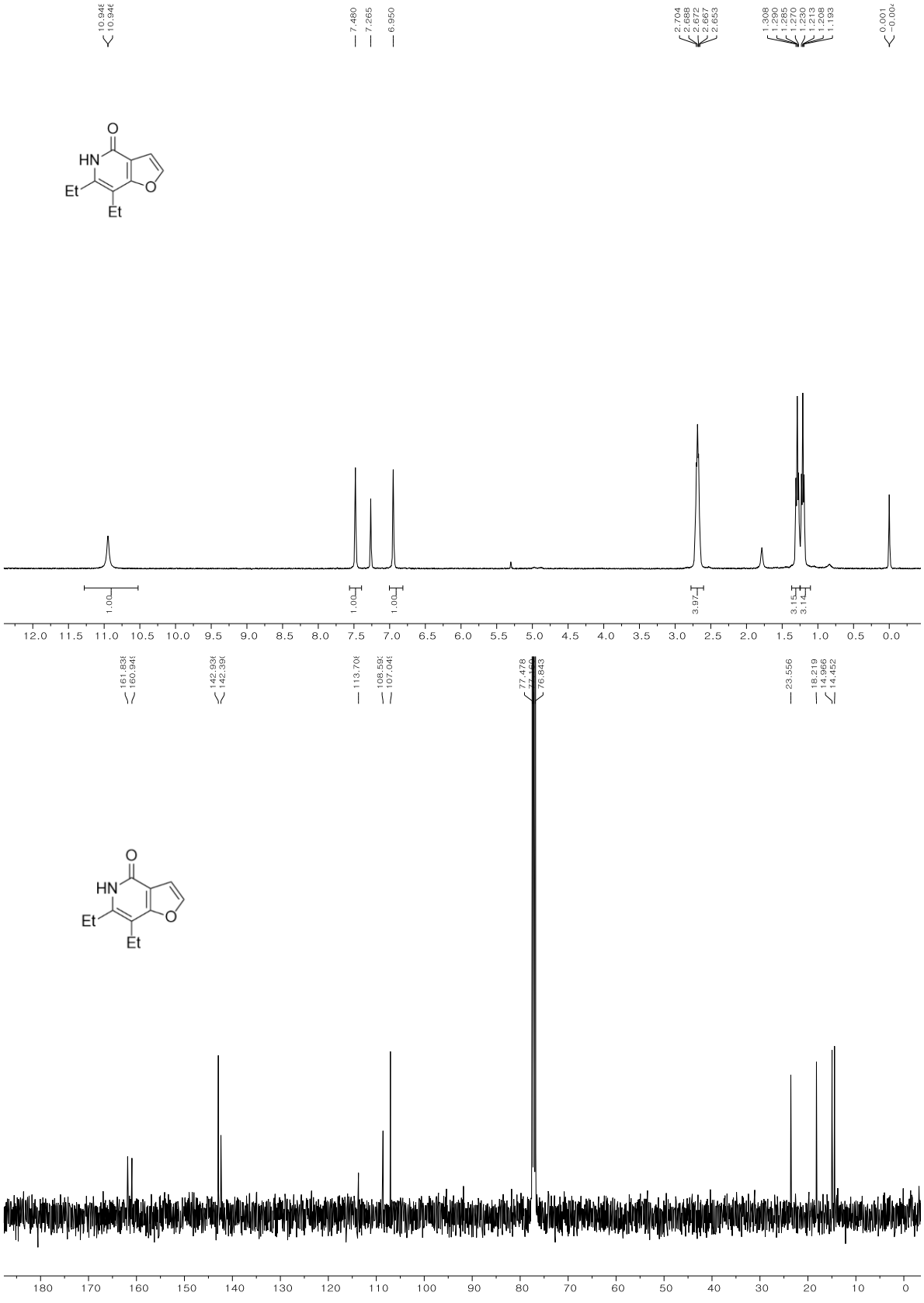
6,7-Diethylthieno[3,2-c]pyridin-4(5H)-one (36).



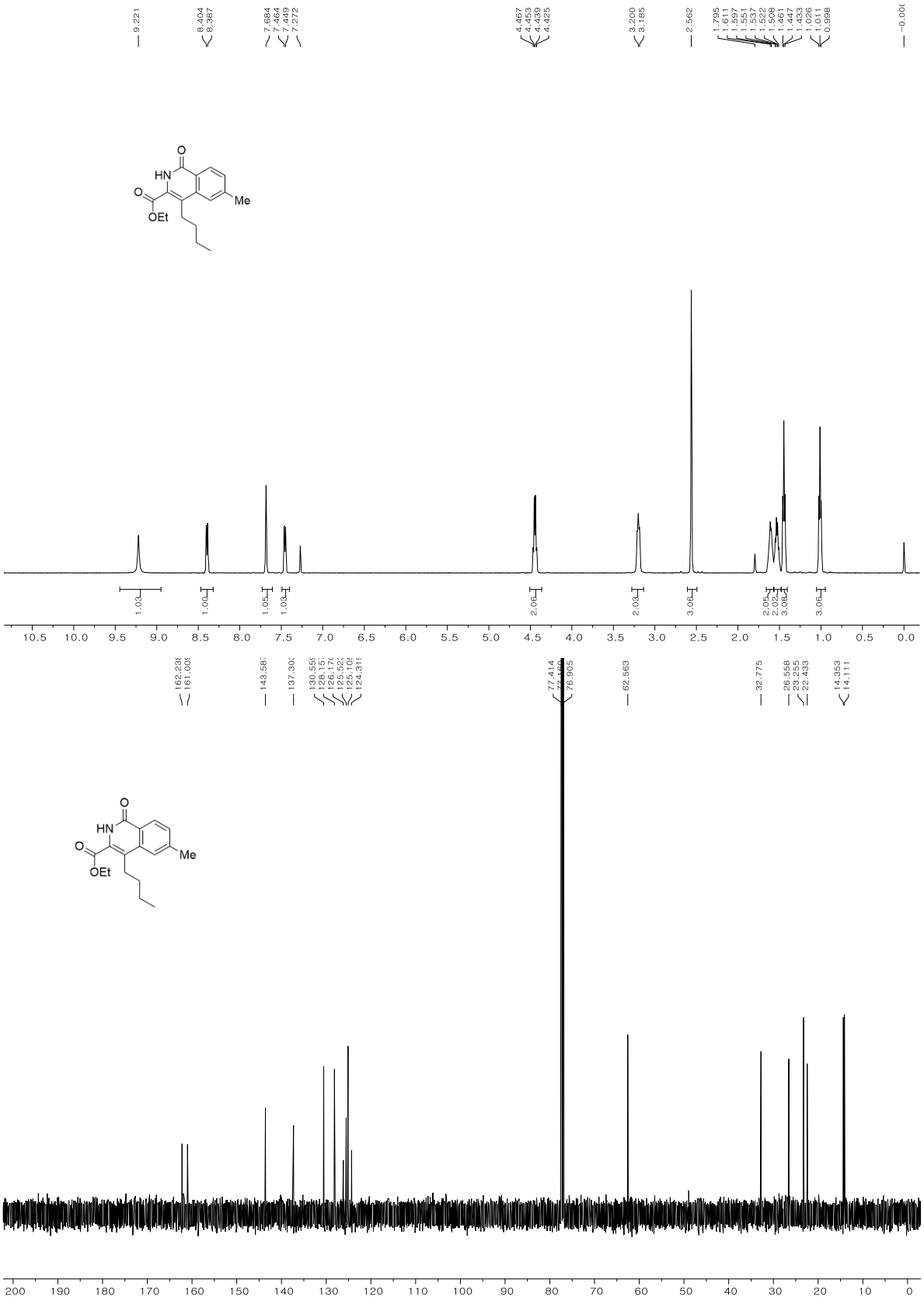
3,4-Diethylbenzo[4,5]thieno[3,2-c]pyridin-1(2H)-one (37).



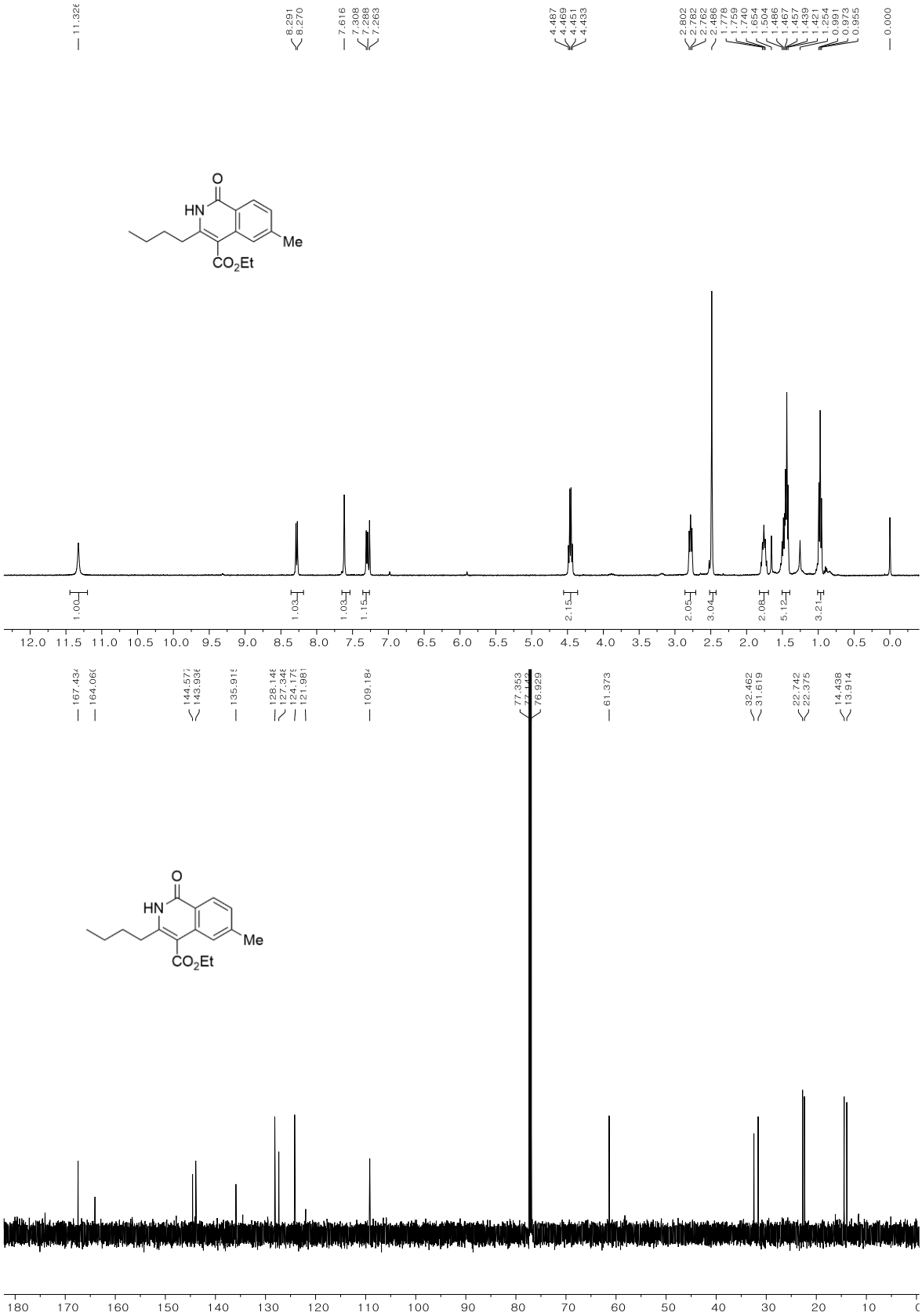
6,7-Diethylfuro[3,2-c]pyridin-4(5H)-one (38).



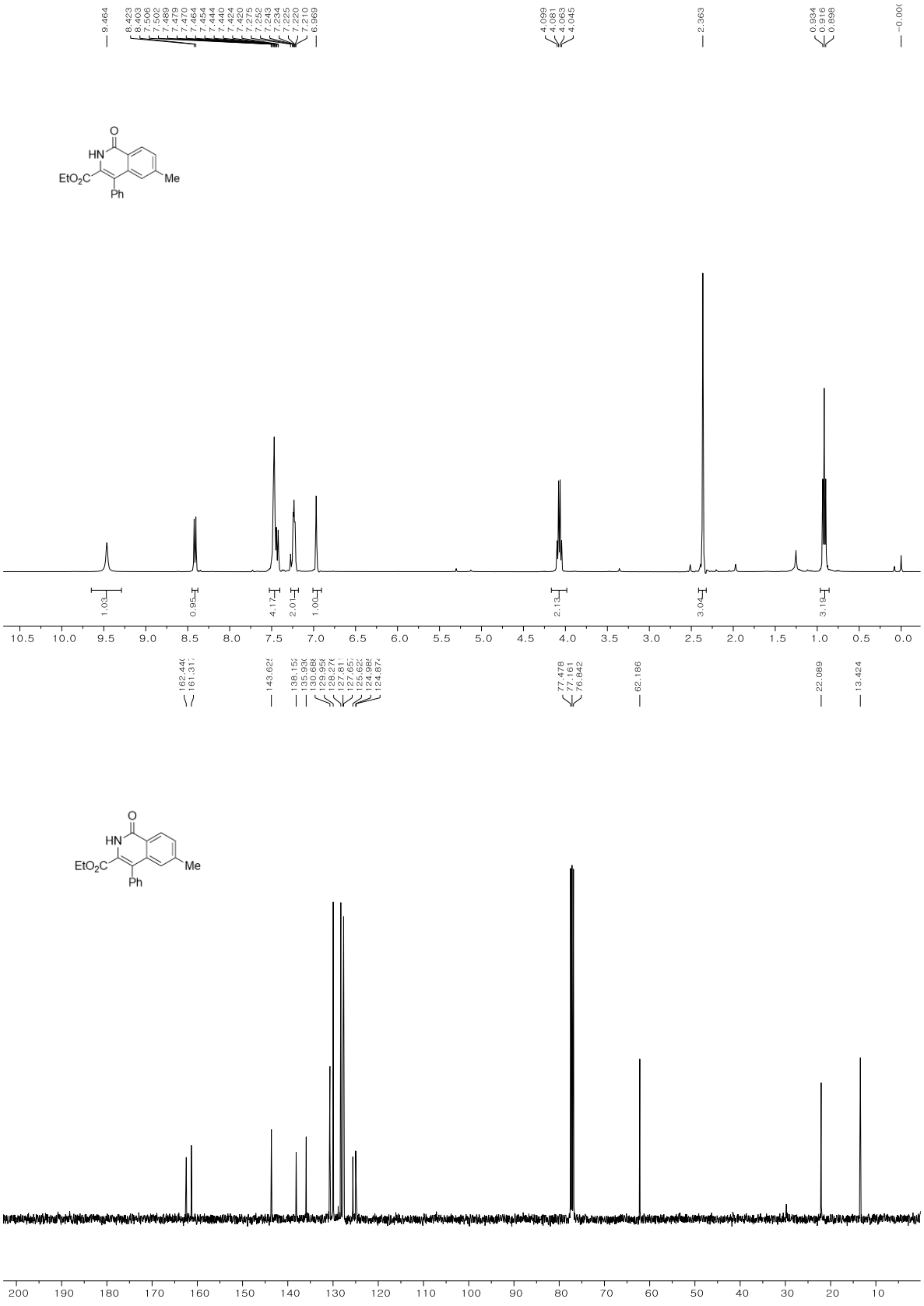
Ethyl 4-butyl-6-methyl-1-oxo-1,2-dihydroisoquinoline-3-carboxylate (39).



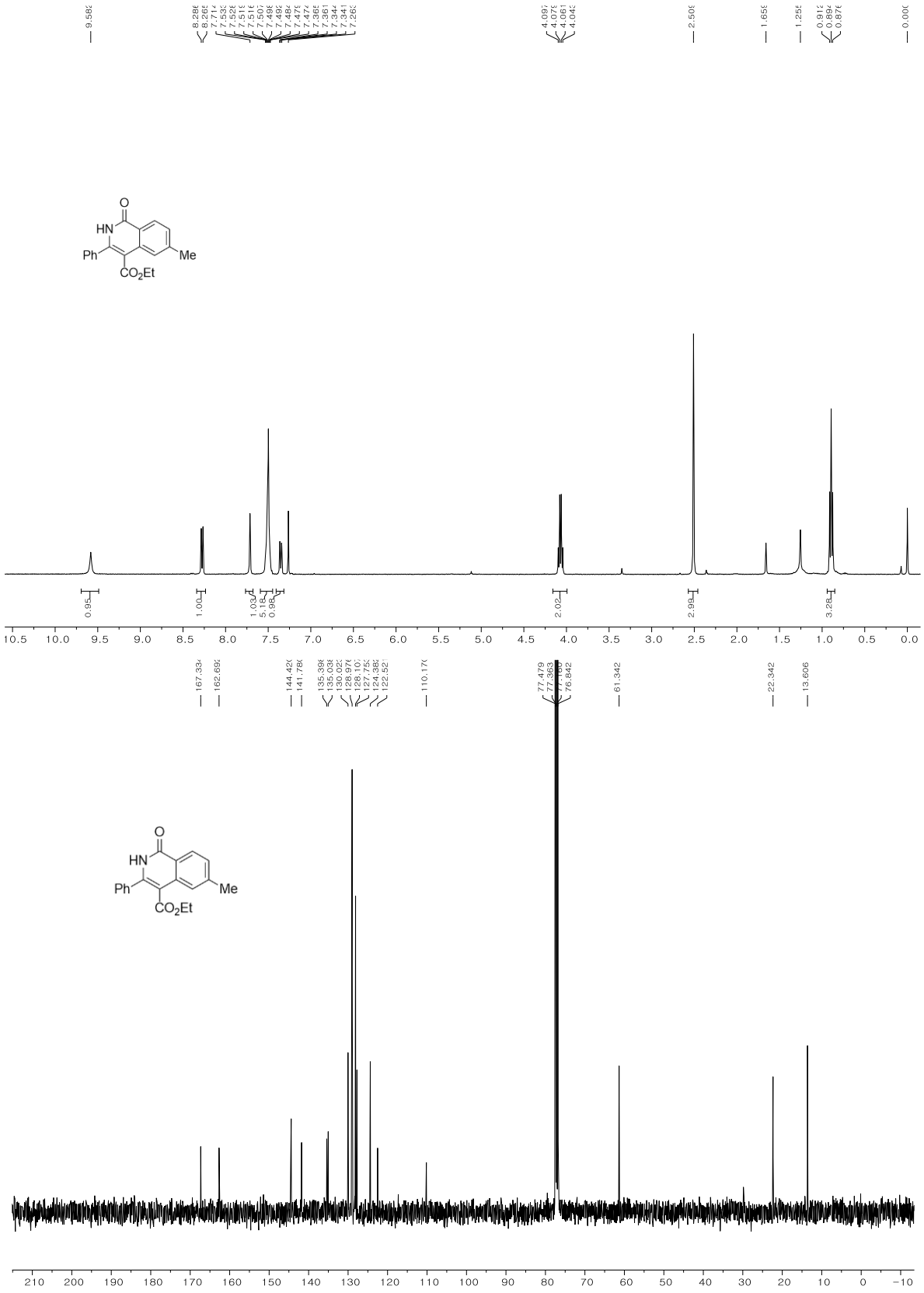
Ethyl 3-butyl-6-methyl-1-oxo-1,2-dihydroisoquinoline-4-carboxylate (40).



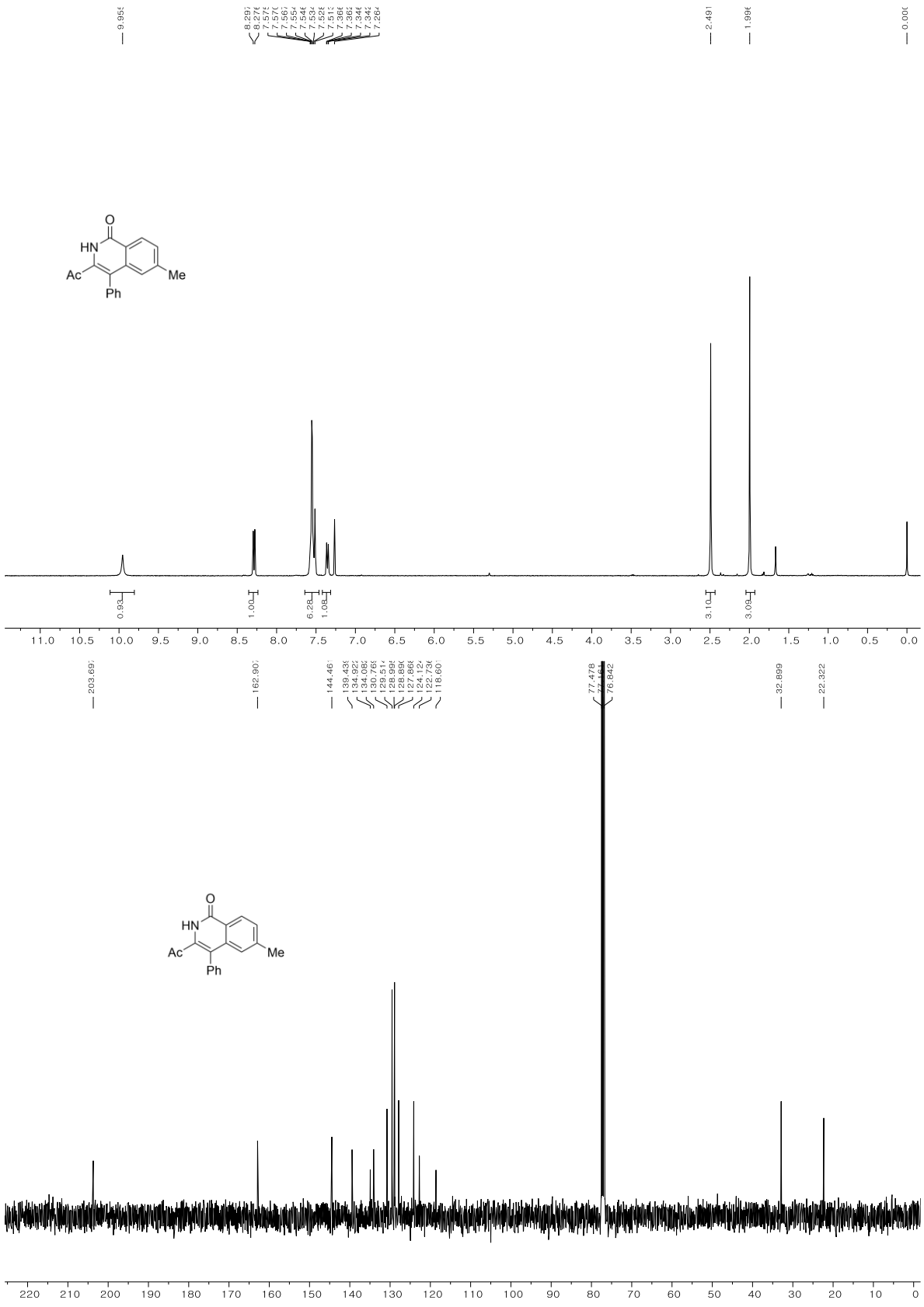
Ethyl 6-methyl-1-oxo-4-phenyl-1,2-dihydroisoquinoline-3-carboxylate (41).



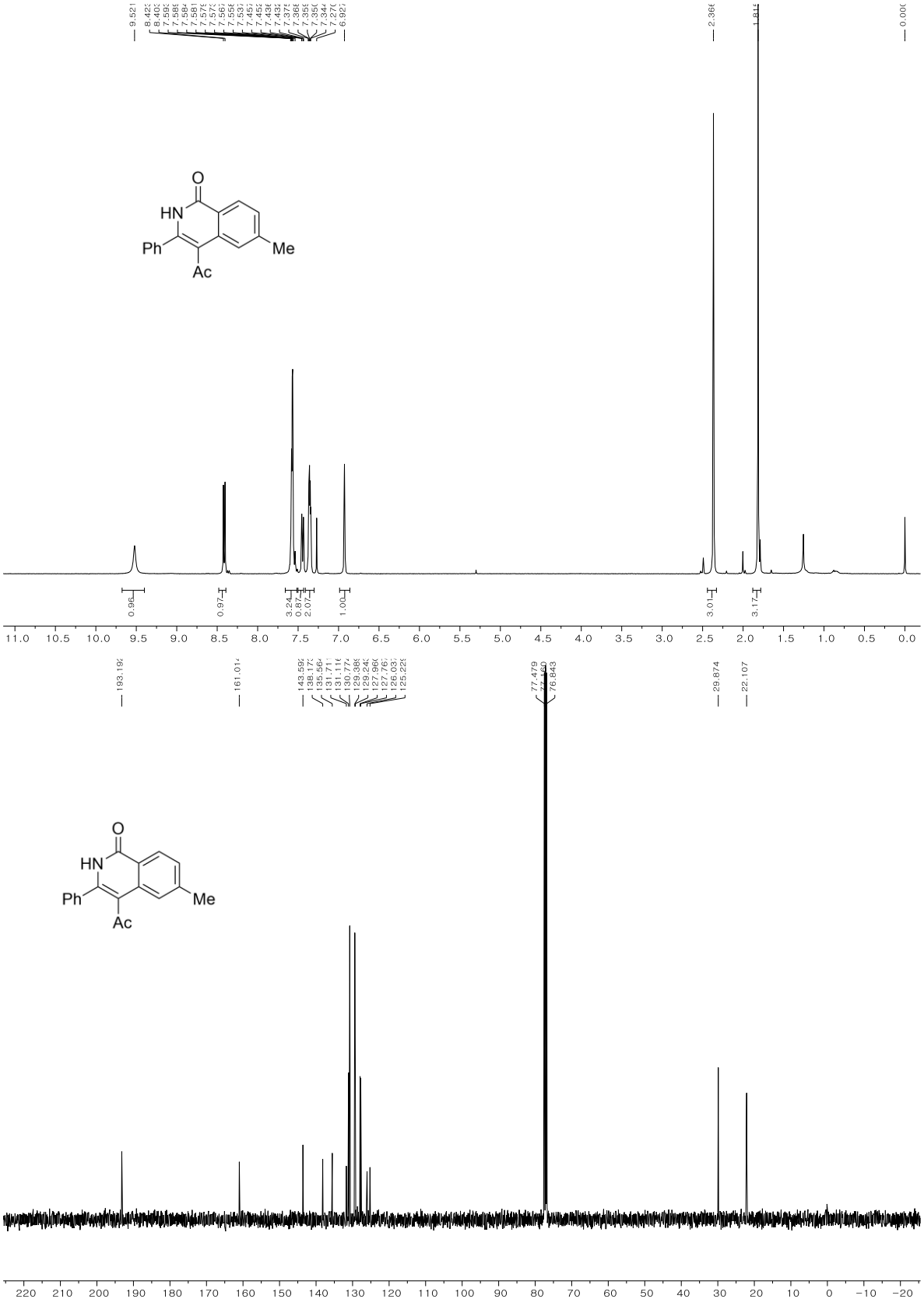
Ethyl 6-methyl-1-oxo-3-phenyl-1,2-dihydroisoquinoline-4-carboxylate (42).



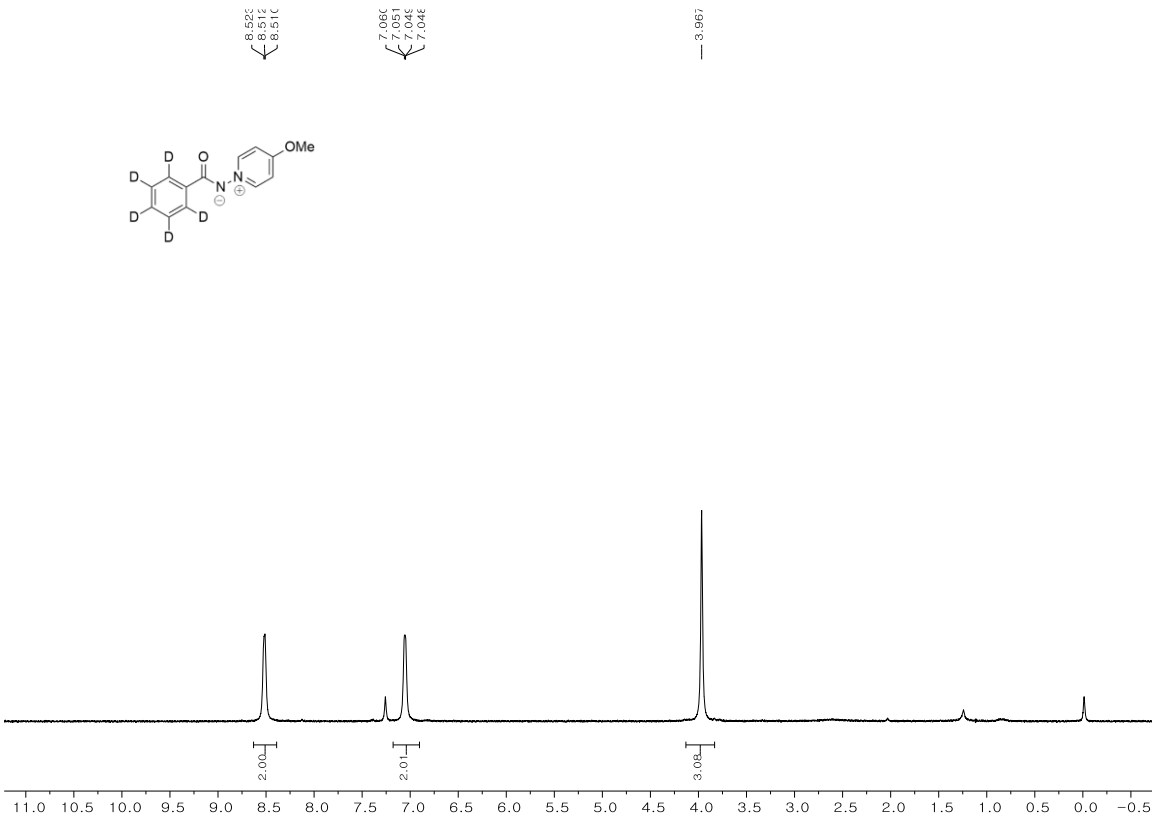
3-Acetyl-6-methyl-4-phenylisoquinolin-1(2H)-one (43).



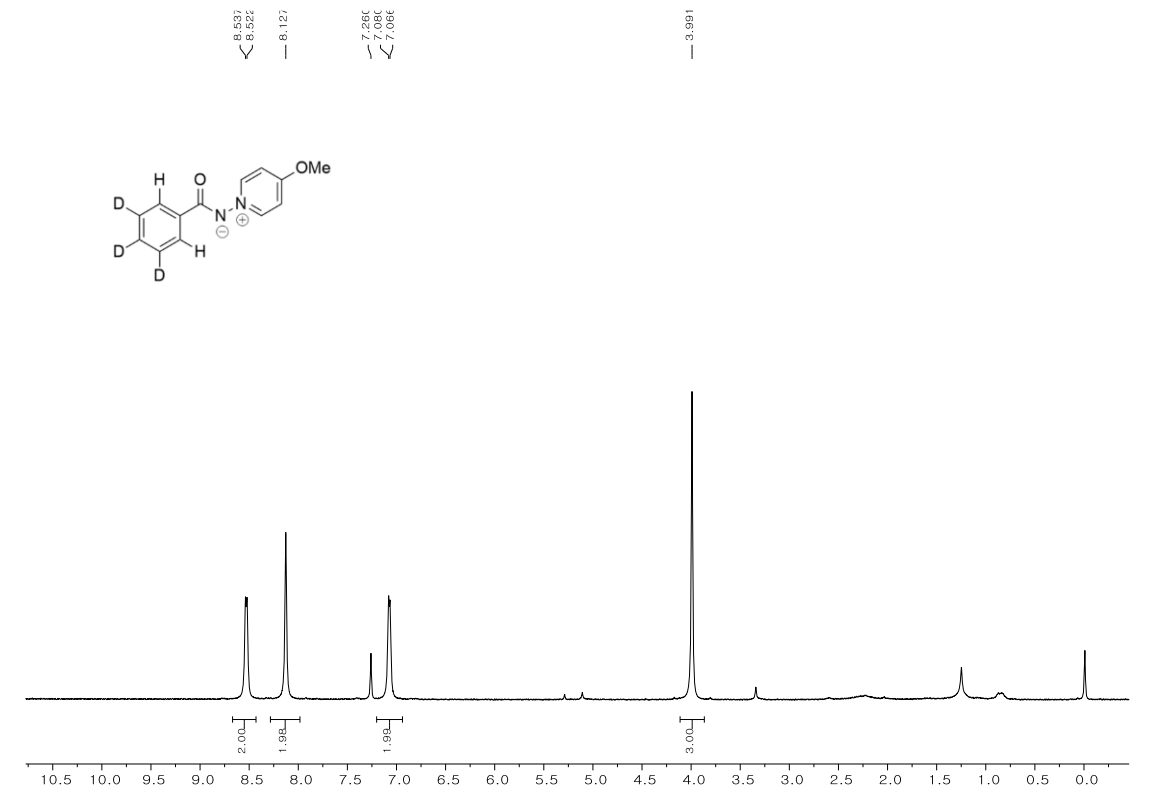
4-Acetyl-6-methyl-3-phenylisoquinolin-1(2H)-one (44).



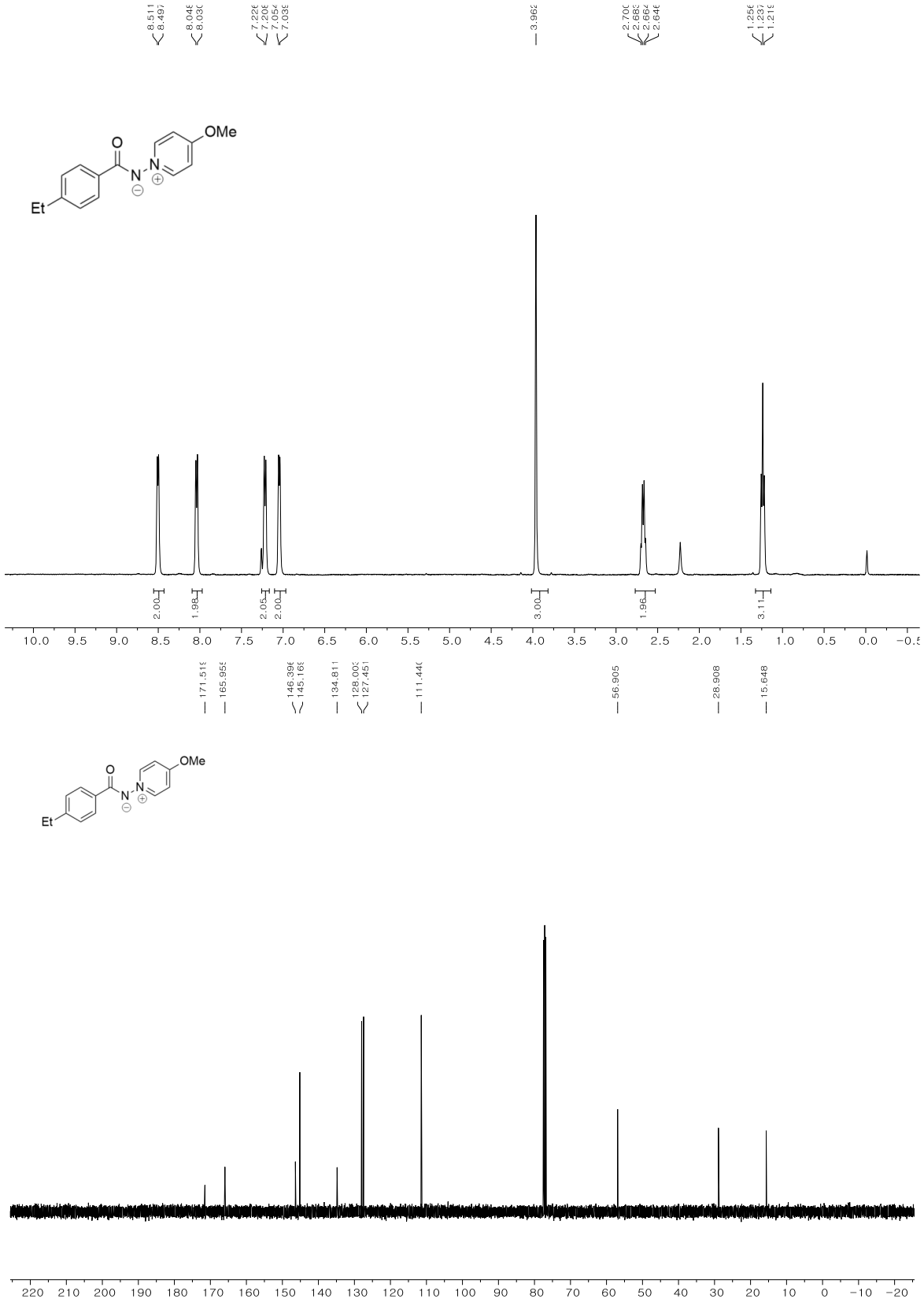
(Benzoyl-2,3,4,5,6-d$_5$)(4-methoxypyridin-1-ium-1-yl)amide (45).



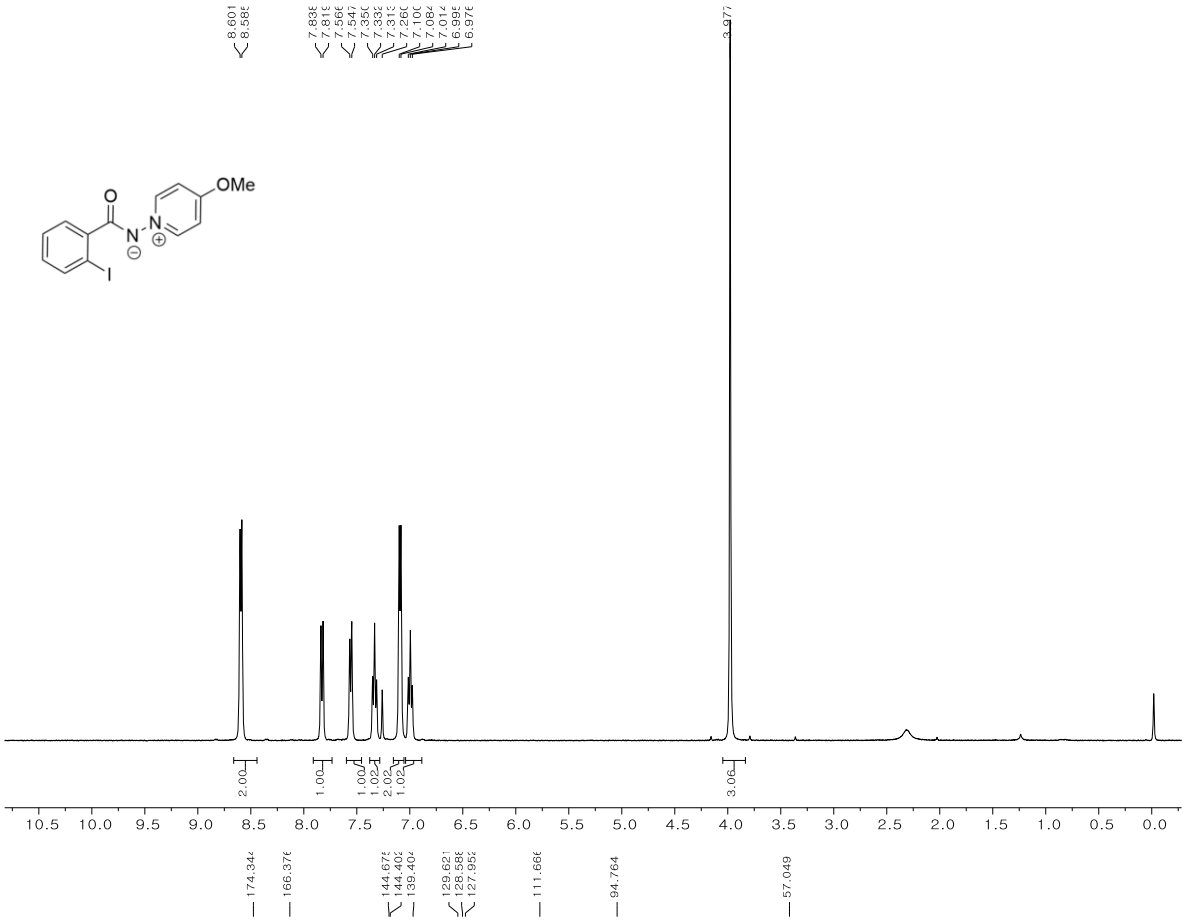
(Benzoyl-3,4,5-d3)(4-methoxypyridin-1-ium-1-yl)amide (45-*d*$_2$).

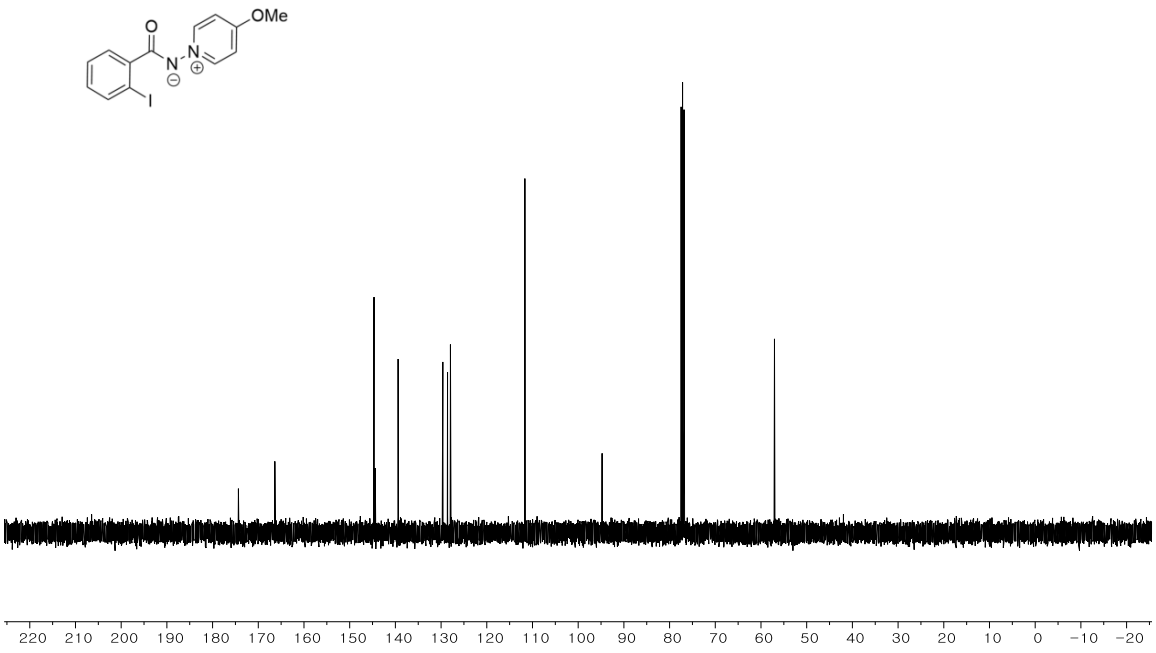


(4-Ethylbenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (47).



(2-Iodobenzoyl)(4-methoxypyridin-1-ium-1-yl)amide (49).





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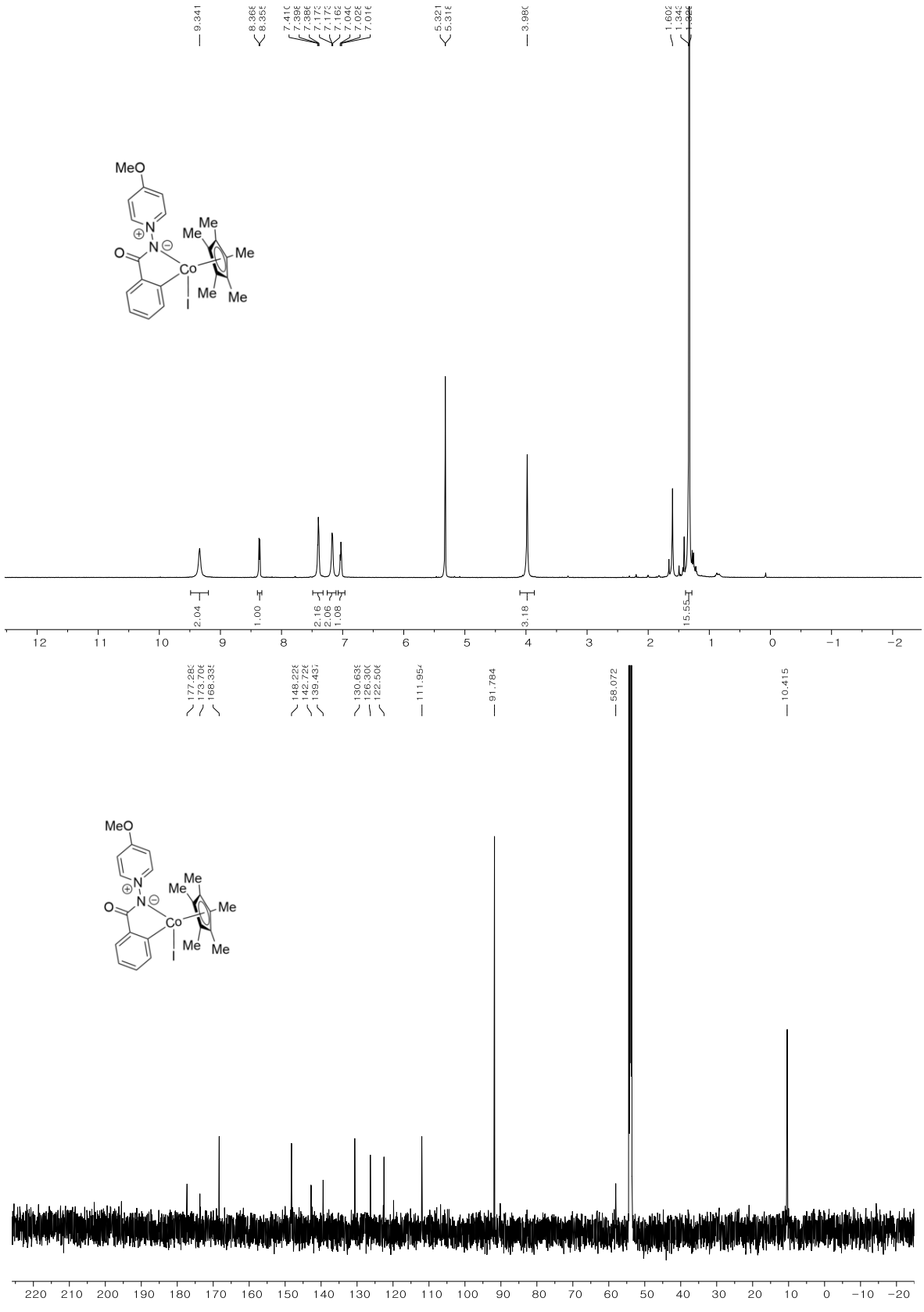
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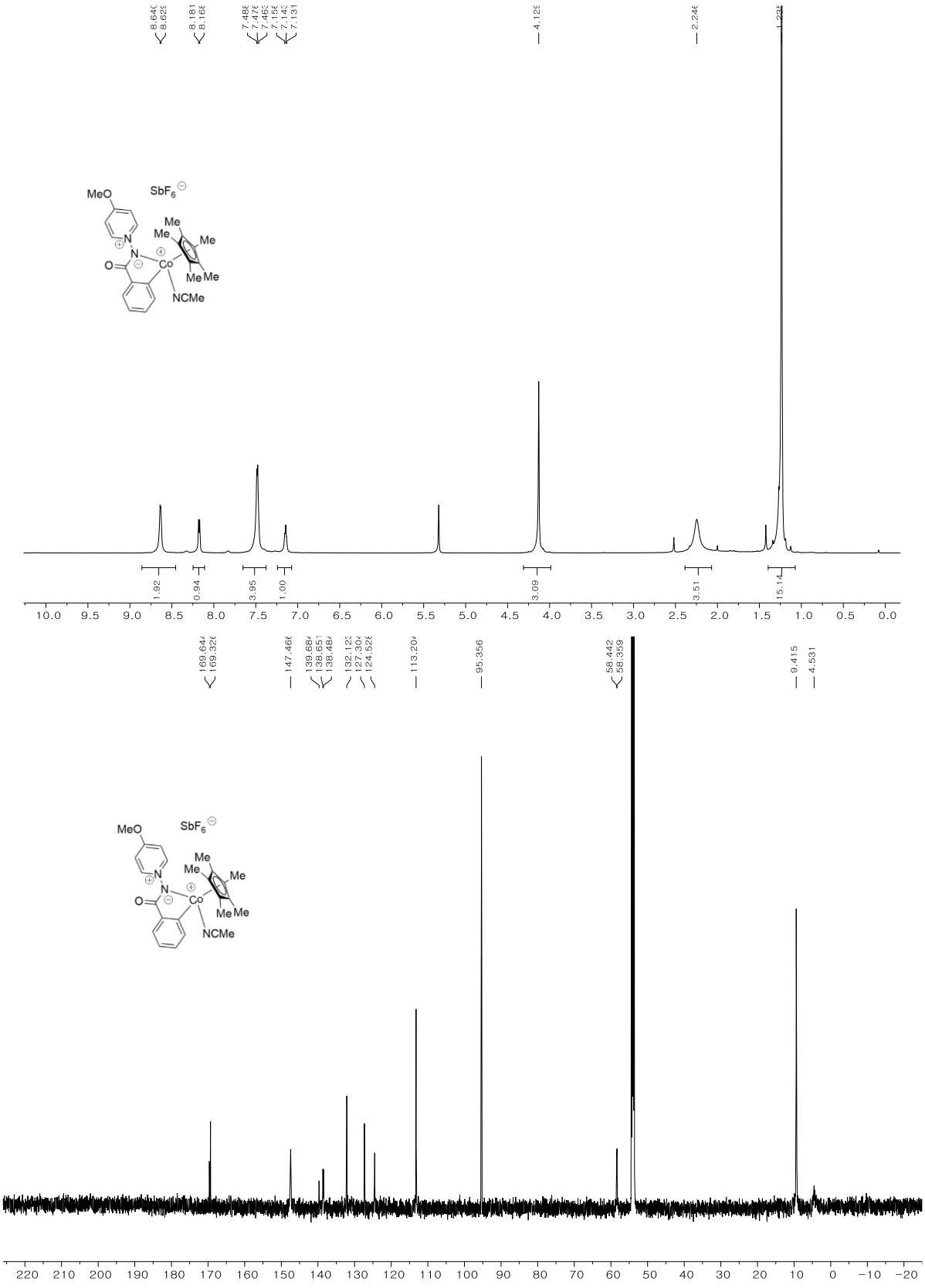
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