Supporting Information for

Azomethine-Isocyanide [3+2] Cycloaddition to Imidazoles Promoted by Silver and DBU

XiaoshanHuang,[a] Xuefeng Cong,[a] Pengbing Mi,[a] and Xihe Bi*[a,b]

[a]*Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Department of Chemistry, Northeast Normal University, Changchun 130024, China.*

[b]*State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China.*

E-mail: bixh507@nenu.edu.cn

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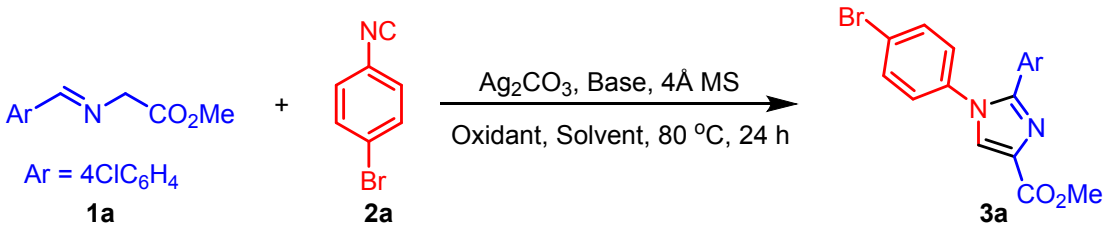
1. General Remarks

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of argon. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.[1] NMR spectra were measured on a Varian I NOVA 500 or Bruker AV-600 spectrometer and reported in parts per million. The ^{1}H-NMR (500 MHz or 600 MHz) chemical shifts were measured relative to TMS, DMSO or $CDCl_3$ as the internal reference. The ^{13}C-NMR (125 MHz or 150 MHz) chemical shifts are given using $CDCl_3$ and DMSO as the internal standard. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Agilent 1200HPLC/MicrOTOF II) equipped with ESI ionization source. Melting points were determined with XRC-1 and are uncorrected.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, and other commercial suppliers and used as received. Solvents were dried over CaH_2 (for DCE and DMF) or sodium (for toluene and 1,4-dioxane) by refluxing for overnight and freshly distilled prior to use. Isocyanides[2] and α-imino esters[3] were prepared according to the corresponding literatures.

2. Optimizing Reaction Parameters

Table S1 Optimization of the Reaction Conditions[a]

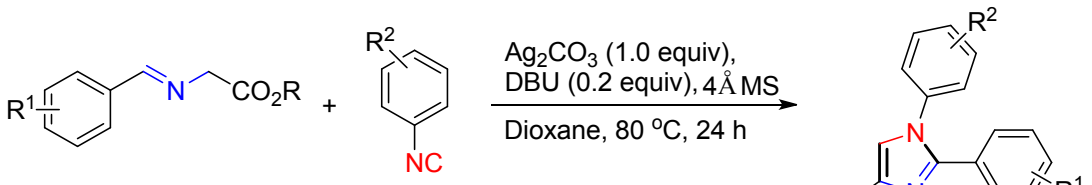


Entry	Base	Oxidant	Solvent	yield of **3a**[b]
1	DBU	-	1,4-Dioxane	72%

2	KOH	-	1,4-Dioxane	13%
3	K_2CO_3	-	1,4-Dioxane	17%
4	Et_3N	-	1,4-Dioxane	23%
5	DABCO	-	1,4-Dioxane	23%
6	DBU	-	DCE	38%
7	DBU	-	toluene	35%
8	DBU	-	DMF	trace
9	DBU	$PhI(OAc)_2$	1,4-Dioxane	nd
10	DBU	$K_2S_2O_8$	1,4-Dioxane	52%
11	DBU	1 atm O_2	1,4-Dioxane	65%
12[c]	DBU	-	1,4-Dioxane	78% (76%)
13[d]	DBU	-	1,4-Dioxane	87% (82%)
14[e]	DBU	-	1,4-Dioxane	85%

[a]Reaction conditions: **1a** (0.75 mmol), **2a** (0.5 mmol), Ag_2CO_3 (30 mol %), base (20 mol %), 4Å MS (200.0 mg) in solvent (5 mL) at 80 °C for 24 h under Ar. [b]Determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard; isolated yield are given in parentheses. [c]Ag_2CO_3 (0.5 equiv) was used. [d]Ag_2CO_3 (1.0 equiv) was used. [e]Ag_2CO_3 (1.2 equiv) was used.

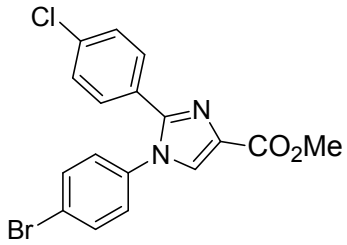
3. General Procedure for the Silver-Promoted Azomethine-Isocyanide [3+2] Cycloaddition



1 **2** **3**

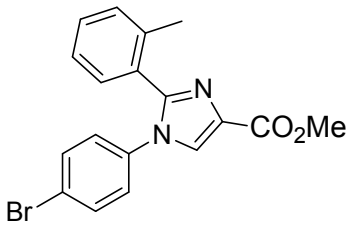
To a dried Schlenk flask, α-imino esters **1** (0.75 mmol), isocyanides **2** (0.5 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) were added under air atmosphere. After evacuated and refilled with nitrogen 3 times, 1,4-dioxane (5 mL), DBU (15.2 μL, 0.01 mmol) was added in one portion to the mixture by syringe. The resulting mixture was stirred at 80 ºC for 24 h. After cooling to room temperature, the reaction mixture was diluted with 5 mL of CH_2Cl_2 and filtered through a plug of celite, followed by washing with 10–20 mL of CH_2Cl_2. The combined residue was

concentrated under reduced pressure, and then the resulting crude product was purified by column chromatography on silica gel to provide the product **3** or **4**.



Methyl 1-(4-bromophenyl)-2-(4-chlorophenyl)-1H-imidazole-4-carboxylate (3a)

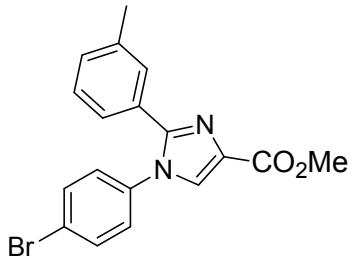
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-chlorobenzylidene)amino)acetate (**1a**) (158.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a slight yellow solid (160.0 mg, 82% yield). Melting point: 146–148 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.81 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 14.8 Hz, 2H), 7.50 (d, J = 14.8 Hz, 2H), 7.33 (s, 2H), 4.17 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 163.0, 146.5, 136.2, 135.5, 133.5, 133.0, 130.1, 128.6, 128.2, 127.2, 127.1, 123.0, 51.9; **HRMS** (ESI^+): calcd for $C_{17}H_{13}BrClN_2O_2$ $[M+H]^+$ 390.9843, found 390.9848.



Methyl 1-(4-bromophenyl)-2-(o-tolyl)-1H-imidazole-4-carboxylate（3b）

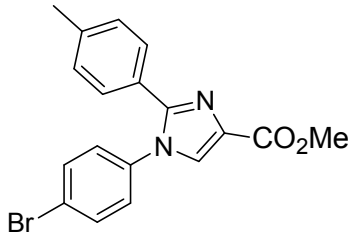
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((2-methylbenzylidene)amino)acetate (**1b**) (143.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (126.0 mg, 68% yield). Melting point: 124–126 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ =

7.90 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.32–7.23 (m, 2H), 7.15 (dd, *J* = 7.8, 1.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H), 2.04 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.3, 147.7, 137.7, 136.1, 133.5, 132.6, 130.9, 130.3, 129.8, 129.1, 126.2, 126.0, 125.7, 122.1, 51.8, 19.8; **HRMS** (ESI^+) m/z calculated for $C_{18}H_{16}BrN_2O_2$ $[M+H]^+$ 371.0390, found 371.0395.



Methyl 1-(4-bromophenyl)-2-(m-tolyl)-1H-imidazole-4-carboxylate (3c)

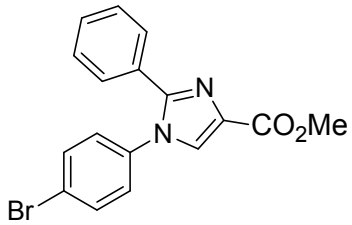
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((3-methylbenzylidene)amino)acetate (**1c**) (143.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a slight yellow solid (156.0 mg, 86% yield). Melting point: 170–171 °C; **^{1}H-NMR**(600 MHz, $CDCl_3$) : δ = 7.81 (s, 1H), 7.55 (d, *J* = 9.0 Hz, 2H), 7.44 (s, 1H), 7.15–7.09 (m, 4H), 6.99 (d, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 2.30 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.2, 147.9, 138.2, 136.6, 133.5, 132.8, 130.0, 129.9, 128.7, 128.0, 127.9, 127.1, 125.8, 122.6, 51.8, 21.2; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}BrN_2O_2$ $[M+H]^+$ 371.0390, found 371.0394.



Methyl 1-(4-bromophenyl)-2-(m-tolyl)-1H-imidazole-4-carboxylate (3d)

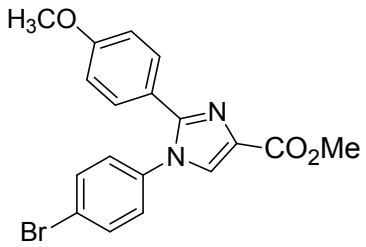
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methylbenzylidene)amino)acetate (**1d**) (143.0 mg, 0.75

mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (155.0 mg, 84% yield). Melting point: 132–133 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.48 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.02 (t, J = 8.4 Hz, 4H), 3.87 (s, 3H), 2.26 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.3, 147.9 139.4 136.7 133.5 132.8 129.0 128.9 127.9 127.2 126.0 122.7, 51.8, 21.2; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}BrN_2O_2$ $[M+H]^+$ 371.0390, found 371.0392.



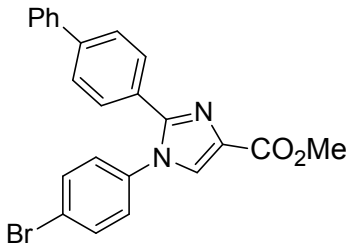
Methyl 1-(4-bromophenyl)-2-phenyl-1H-imidazole-4-carboxylate (3e)

The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-(benzylideneamino)acetate (**1e**) (133.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (142.0 mg, 80% yield). Melting point: 162–163 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.74 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.2 Hz, 2H), 7.25 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.2, 147.7, 136.5, 133.6, 132.8, 129.2, 129.0, 128.8, 128.3, 128.0, 127.2, 122.7, 51.8; **HRMS** (ESI^+) m/z calcd for $C_{17}H_{14}BrN_2O_2$ $[M+H]^+$ 357.0233, found 357.0236.



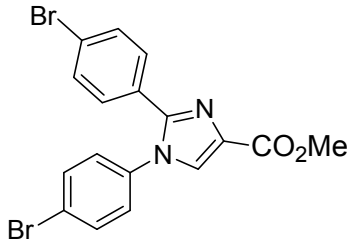
Methyl 1-(4-bromophenyl)-2-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (3f)

The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (166.0 mg, 86% yield). Melting point: 166–167 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H), 2.04 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.2, 160.3, 147.6, 136.6, 133.3, 132.8, 130.4, 127.7, 127.2, 122.6, 121.3, 113.7, 55.16, 51.74; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}BrN_2O_3$ $[M+H]^+$ 387.0348, found 387.0339.



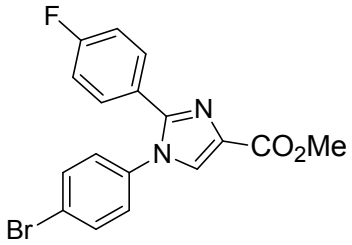
Methyl 2-([1,1'-biphenyl]-4-yl)-1-(4-bromophenyl)-1H-imidazole-4-carboxylate (3g)

The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-(([1,1'-biphenyl]-4-ylmethylene)amino)acetate (**1g**) (190.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (184.0 mg, 85% yield). Melting point: 190-191 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.74 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.1, 147.4, 141.8, 139.8, 136.5, 133.6, 132.9, 129.3, 128.8, 128.2, 127.7, 127.6, 127.2, 126.9, 126.8, 122.8, 51.8; **HRMS** (ESI^+) m/z calcd for $C_{23}H_{18}BrN_2O_2$ $[M+H]^+$ 434.0552, found 434.0555.



Methyl 1,2-bis(4-bromophenyl)-1H-imidazole-4-carboxylate (3h)

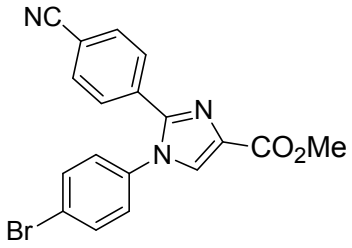
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-bromobenzylidene)amino)acetate (**1h**) (191.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a slight yellow solid (170.0 mg, 78% yield). Melting point: 169-170 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 3.94 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.0, 146.5, 136.2, 133.7, 133.1, 131.5, 130.4, 128.3, 127.7, 127.2, 123.8, 123.0, 51.9; **HRMS** (ESI^+) m/z calcd for $C_{17}H_{12}Br_2N_2NaO_2$ $[M+Na]^+$ 456.9158, found 456.9166.



Methyl 1-(4-bromophenyl)-2-(4-fluorophenyl)-1H-imidazole-4-carboxylate (3i)

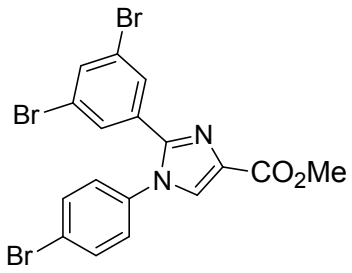
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-fluorobenzylidene)amino)acetate (**1i**) (146.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (169.0 mg, 90% yield). Melting point: 181-183 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.40–7.38 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 8.4 Hz, 2H), 3.94 (s, 3H);**^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.9 (t, J = 135 Hz, 1C), 163.0, 146.7, 136.3, 133.5, 132.9, 130.99 (d, J = 9 Hz, 1C), 128.0, 127.1, 125.0 (d, J =

22.5 Hz, 1C), 122.9, 115.5 (d, J = 22.5 Hz, 1C), 51.8; **HRMS** (ESI^+) m/z calcd for $C_{17}H_{12}BrFNaN_2O_2$ $[M+Na]^+$ 396.9958, found 396.9934.



Methyl 1-(4-bromophenyl)-2-(4-cyanophenyl)-1H-imidazole-4-carboxylate (3j)

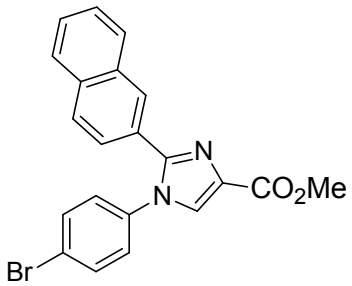
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-cyanobenzylidene)amino)acetate (**1j**) (152.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (88.0 mg, 46% yield). Melting point: 171-172 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.56 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 3.90 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 162.7, 145.4, 135.9, 134.2, 133.3, 133.0, 132.1, 129.2, 128.9, 127.1, 123.5, 118.1, 112.8, 52.0; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{13}BrN_3O_2$ $[M+H]^+$ 382.0186, found 382.0193.



Methyl 1-(4-bromophenyl)-2-(3,5-dibromophenyl)-1H-imidazole-4-carboxylate (3k)

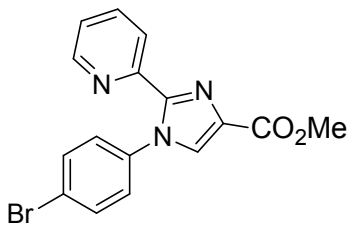
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((3,5-dibromobenzylidene)amino)acetate (**1k**) (250.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid

(151.0 mg, 59% yield). Melting point:185-187 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.70–7.57 (m, 3H), 7.50 (d, J = 1.8 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 3.96 (s, 3H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 162.8, 144.5, 135.7, 134.7, 133.9, 133.2, 132.0, 130.4, 128.6, 127.1, 123.5, 122.8, 52.0; **HRMS** (ESI^+) m/z calcd for $C_{17}H_{12}Br_3N_2O_2$ $[M+H]^+$ 512.8443, found 512.8444.



Methyl 1-(4-bromophenyl)-2-(naphthalen-2-yl)-1H-imidazole-4-carboxylate (3l)

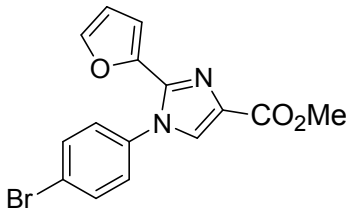
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((naphthalen-2-ylmethylene)amino)acetate (**1l**) (170.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (189.0 mg, 93% yield). Melting point: 155–157 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.86 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.52–7.44 (m, 2H), 7.39 (dd, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 9.0 Hz, 2H), 3.97 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.3, 147.7, 136.6, 133.8, 133.3, 133.0, 132.8, 129.1, 128.5, 128.2, 127.9, 127.6, 127.2, 127.1, 126.6, 126.2, 125.7, 122.8, 51.5; **HRMS** (ESI^+) m/z calcd for $C_{21}H_{16}BrN_2O_2$ $[M+H]^+$ 407.0390 , found 407.0399



Methyl 1-(4-bromophenyl)-2-(pyridin-2-yl)-1H-imidazole-4-carboxylate (3m)

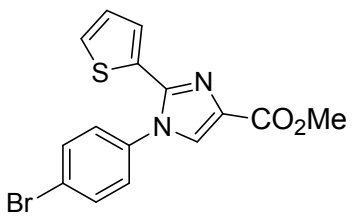
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5

mmol), (*E*)-methyl 2-((pyridin-2-ylmethylene)amino)acetate (**1m**) (134.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (100.0 mg, 56% yield). Melting point: 138–140 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 8.28 (d, J = 4.2 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.81 (s, 1H), 7.75 (td, J = 7.8, 1.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.21–7.20 (m, 1H), 7.15 (d, J = 9.0 Hz, 2H), 3.95 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.0, 148.4, 148.3, 146.0, 137.6, 136.5, 133.2, 132.1, 129.3, 127.4, 123.8, 123.5, 122.2, 51.9; **HRMS** (ESI^+) m/z calcd for $C_{16}H_{13}BrN_3O_2$ $[M+H]^+$ 358.0186, found 358.0195.



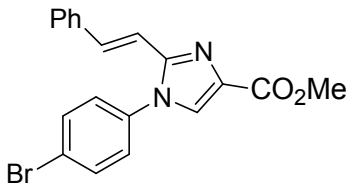
Methyl 1-(4-bromophenyl)-2-(furan-2-yl)-1H-imidazole-4-carboxylate (3n)

The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (E)-methyl 2-((furan-2-ylmethylene)amino)acetate (**1n**) (125.0 mg, 0.75 mmol), DBU (15.2 μl, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (101.0 mg, 58% yield). Melting point: 158-159 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.56 (d, J = 9.0 Hz, 2H), 7.26 (s, 1H), 7.15 (d, J = 9.0 Hz, 2H), 6.38 (d, J = 3.6 Hz, 1H), 6.29 (dd, J = 3.6, 1.8 Hz, 1H), 3.86 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 162.9, 143.5, 143.4, 139.9, 136.0, 133.7, 132.6, 127.6, 123.4, 111.3, 111.2, 51.8; **HRMS** (ESI^+) m/z calcd for $C_{15}H_{12}BrN_2O_3$ $[M+H]^+$ 347.0026, found 347.0020.



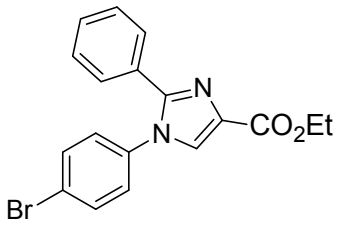
Methyl 1-(4-bromophenyl)-2-(thiophen-2-yl)-1H-imidazole-4-carboxylate (3o)

The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-methyl 2-((thiophen-2-ylmethylene)amino)acetate (**1o**) (137.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (80.0 mg, 44% yield). Melting point: 142-144 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.65 (d, J = 9.0 Hz, 2H), 7.29 (dd, J = 4.2, 1.2 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 6.92–6.87 (m, 2H), 3.93 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ =163.0, 143.1, 135.9, 133.5, 133.0, 130.8, 128.3, 128.0, 127.9, 127.6, 127.2, 123.8, 51.9; **HRMS** (ESI^+) m/z calcd for $C_{15}H_{12}BrN_2O_2S$ $[M+H]^+$ 362.9797, found 362.9787.



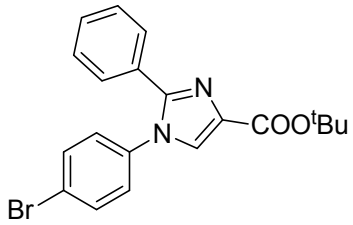
(E)-methyl 1-(4-bromophenyl)-2-styryl-1H-imidazole-4-carboxylate (3p)

The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), methyl 2-((*E*)-((*E*)-3-phenylallylidene)amino)acetate (**1p**) (152.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (67.0 mg, 35% yield). Melting point: 130–132 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.83 (d, J = 16.2 Hz, 1H), 7.75 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.30–7.26 (m, 3H), 6.66 (d, J = 16.2 Hz, 1H), 3.96 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.2, 146.5, 135.9, 135.8, 135.3, 133.7, 133.1, 128.9, 128.8, 127.6, 127.0, 126.9, 123.3, 112.4, 52.0; **HRMS** (ESI^+) m/z calcd for $C_{19}H_{16}BrN_2O_2$ $[M+H]^+$ 383.0390, found 383.0397.



Ethyl 1-(4-bromophenyl)-2-phenyl-1H-imidazole-4-carboxylate (3q)

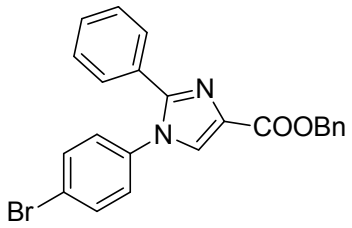
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-ethyl 2-(benzylideneamino)acetate (**1q**) (143.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (158.0 mg, 85% yield). Melting point: 134-135 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 6.6 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.29-7.25 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 162.8, 147.7, 136.6, 133.9, 132.9, 129.2, 129.1, 129.0, 128.3, 128.0, 127.2, 122.7, 60.7, 14.4; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}BrN_2O_2$ $[M+H]^+$ 371.0390, found 371.0394.



Tert-butyl 1-(4-bromophenyl)-2-phenyl-1H-imidazole-4-carboxylate (3r)

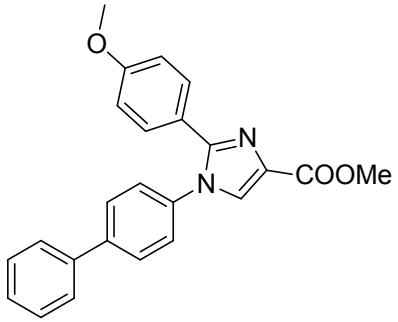
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-tert-butyl 2-(benzylideneamino)acetate (**1r**) (164.0 mg, 0.75 mmol), DBU(15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (138.0 mg, 69% yield). Melting point: 150-152 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 1.54 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ =

162.0, 147.4, 136.8, 135.1, 132.8, 129.1, 129.1, 129.0, 128.2, 127.4, 127.2, 122.6, 81.1, 28.3; **HRMS** (ESI^+) m/z calcd for $C_{20}H_{20}BrN_2O_2$ $[M+H]^+$ 399.0703, found 399.0712.



Benzyl 1-(4-bromophenyl)-2-phenyl-1H-imidazole-4-carboxylate (3s)

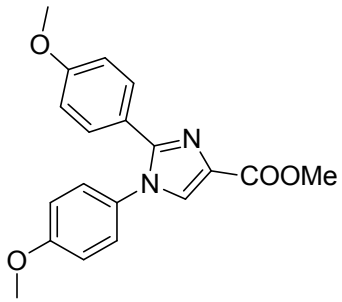
The general procedure was applied to 1-bromo-4-isocyanobenzene (**2a**) (91.0 mg, 0.5 mmol), (*E*)-benzyl 2-(benzylideneamino)acetate (**1s**) (190.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (93.0 mg, 43% yield). Melting point: 132-134 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.44 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 7.29–7.20 (m, 4H), 7.19 (t, J = 7.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 5.31 (s, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 162.4, 147.7, 136.4, 136.0, 133.3, 132.7, 129.2, 128.9, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.1, 122.6, 66.2; **HRMS** (ESI^+) m/z calcd for $C_{23}H_{18}BrN_2O_2$ $[M+H]^+$ 433.0546, found 433.0557.



Methyl 1-([1,1'-biphenyl]-4-yl)-2-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4b)

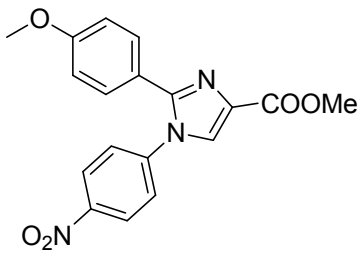
The general procedure was applied to 4-isocyano-1,1'-biphenyl (**2b**) (90.0 mg, 0.5

mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (165.0 mg, 86% yield). Melting point: 172-173 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 9.0 Hz, 3H), 7.29 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 3.95 (s, 3H), 3.79 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.5, 160.2, 147.8, 141.7, 139.4, 136.8, 133.1, 130.5, 129.0, 128.2, 128.0, 127.0, 126.0, 121.7, 113.6, 104.7, 55.2, 51.8; **HRMS** (ESI$^+$) m/z calcd for $C_{24}H_{21}N_2O_3$ $[M+H]^+$ 384.1556, found 384.1564.



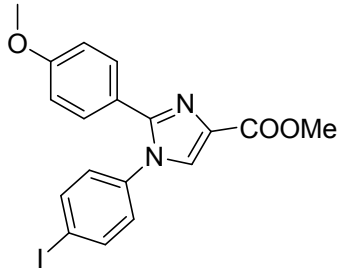
Methyl 1,2-bis(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4c)

The general procedure was applied to 1-isocyano-4-methoxybenzene (**2c**) (67.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μl, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (93.0 mg, 43% yield). Melting point: 122-123 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.38 (d, J = 9.0 Hz, 2H), 7.16 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 3.95 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 176.7, 159.8, 159.1, 147.5, 132.7, 130.5, 130.3, 128.4, 126.9, 121.7, 114.7, 113.2, 56.0, 54.9, 51.4; **HRMS** (ESI$^+$) m/z calcd for $C_{19}H_{19}N_2O_4$ $[M+H]^+$ 339.1339, found 339.1349.



Methyl 2-(4-methoxyphenyl)-1-(4-nitrophenyl)-1H-imidazole-4-carboxylate (4d)

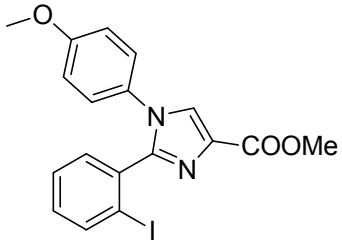
The general procedure was applied to 1-isocyano-4-nitrobenzene (**2d**) (77.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (115.0 mg, 65% yield). Melting point: 147-148 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 8.28 (d, J = 9.0 Hz, 2H), 7.86 (s, 1H), 7.40 (d, J = 9.0 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H), 3.79 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.0, 160.6, 147.8, 147.2, 142.6, 134.0, 130.6, 127.2, 126.2, 125.1, 120.7, 114.0, 55.2, 51.9; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}N_3O_5$ $[M+H]^+$ 354.1084, found 354.1091.



Methyl 1-(4-iodophenyl)-2-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4e)

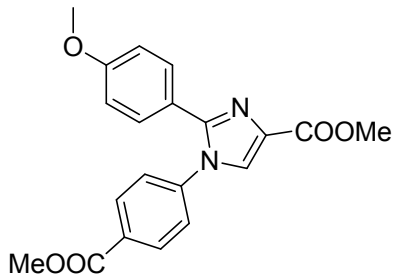
The general procedure was applied to 1-iodo-4-isocyanobenzene (**2e**) (65.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (169.0 mg, 78% yield). Melting point: 175-177 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ =

7.69 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H), 3.70 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.2, 160.2, 147.5, 138.7, 137.3, 133.3, 130.3, 127.6, 127.3, 121.2, 113.6, 93.9, 55.1, 51.7; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}IN_2O_3$ $[M+H]^+$ 435.0200, found 435.0209.



Methyl 2-(2-iodophenyl)-1-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4f)

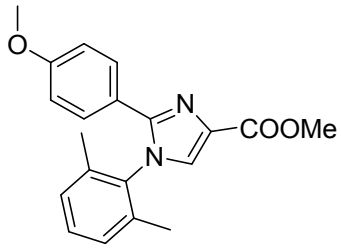
The general procedure was applied to 1-iodo-2-isocyanobenzene (**2f**) (115.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (160.0 mg, 74% yield). Melting point: 169-171 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.8 Hz, 1H), 7.70 (s, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 9.0 Hz, 2H), 3.95 (s, 3H), 3.76 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.3, 160.1, 147.8, 140.5, 140.2, 133.0, 130.9, 129.8, 129.4, 128.6, 128.0, 121.7, 113.5, 97.1, 55.1, 51.7; **HRMS** (ESI^+) m/z calcd for $C_{18}H_{16}IN_2O_3$ $[M+H]^+$ 435.0200, found 435.0209.



Methyl 1-(4-(methoxycarbonyl)phenyl)-2-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4g)

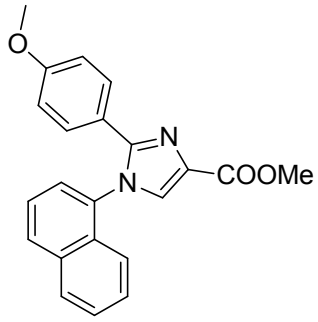
The general procedure was applied to methyl 4-isocyanobenzoate (**2g**) (80.0 mg, 0.5

mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (88.0 mg, 48% yield). Melting point: 124-125 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.4 Hz, 2H), 7.86 (s, 1H), 7.31–7.29 (m, 4H), 6.77 (d, J = 9.0 Hz, 2H), 3.95 (s, 6H), 3.78 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 165.7, 163.3, 160.4, 147.8, 141.2, 133.4, 131.0, 130.5, 130.3, 127.6, 125.5, 121.1, 113.7, 77.2, 77.0, 76.7, 55.2, 52.4, 51.9; **HRMS** (ESI^+) m/z calcd for $C_{20}H_{19}N_2O_5$ $[M+H]^+$ 367.1288, found 367.1300.



Methyl 1-(2,6-dimethylphenyl)-2-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4h)

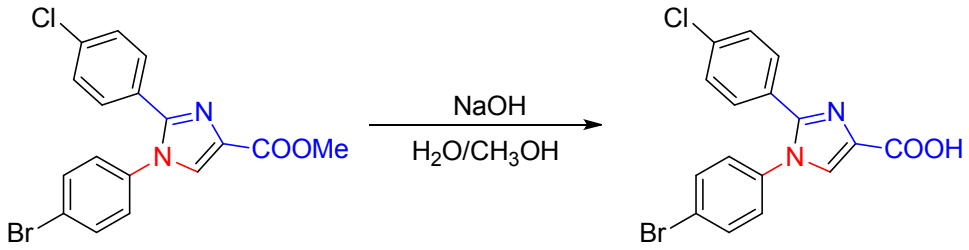
The general procedure was applied to 2-isocyano-1,3-dimethylbenzene (**2h**) (65.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (125.0 mg, 65% yield). Melting point: 137-138 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.29 (d, J = 9.0 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.5 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.68 (s, 3H), 1.90 (s, 6H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.5, 160.1, 147.5, 136.2, 135.2, 133.3, 129.4, 128.7, 128.7, 127.4, 122.0, 113.6, 55.0, 51.7; **HRMS** (ESI^+) m/z calcd for $C_{20}H_{21}N_2O_3$ $[M+H]^+$ 337.1547, found 337.1544.



Methyl 2-(4-methoxyphenyl)-1-(naphthalen-1-yl)-1H-imidazole-4-carboxylate (4i)

The general procedure was applied to 1-isocyanonaphthalene (**2i**) (77.0 mg, 0.5 mmol), (*E*)-methyl 2-((4-methoxybenzylidene)amino)acetate (**1f**) (155.0 mg, 0.75 mmol), DBU (15.2 μL, 0.01 mmol), 200 mg 4Å MS and Ag_2CO_3 (138.0 mg, 0.5 mmol) at 80 ºC for 24 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/12) to afford the title compound as a slight yellow solid (122.0 mg, 68% yield). Melting point: 151-152 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.44–7.38 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H), 3.58 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ = 163.4, 159.9, 148.9, 134.1, 134.0, 133.0, 129.8, 129.5, 129.5, 129.4, 128.3, 127.9, 127.0, 125.2, 125.1, 122.1, 121.5, 113.4, 55.0, 51.7; **HRMS** (ESI^+) m/z calcd for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1390, found 359.1400.

4. Synthetic Applications



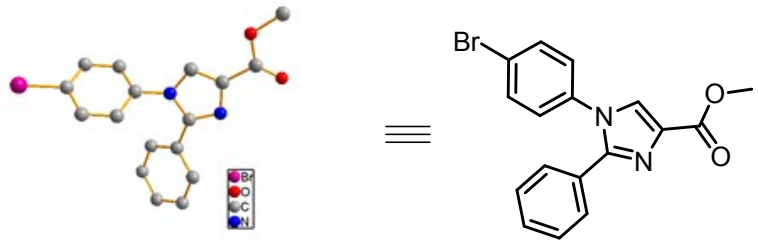
3a **3aa**, 83%

1-(4-bromophenyl)-2-(4-chlorophenyl)-1H-imidazole-4-carboxylic acid (3aa)[4]

A mixture of ester **3a** (0.784 g, 2 mmol) in CH_3OH (14 mL) and NaOH (1 N aqueous solution, 14 mL) was refluxed for 1.5 h. After cooled to room temperature, the mixture was concentrated under vacuum. The residue was solubilized in water and then acidified with concentrated HCl (pH = 2). The resulting mixture was extracted with CH_2Cl_2 (3 x 15 mL), and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was triturated with ether to give pure product **3aa** as a slight yellow solid (0.626 g, 83%). Melting point: 124–125 °C; **^{1}H-NMR** (600 MHz, DMSO): δ = 12.47 (s, 1H), 8.14 (s, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 4H); **^{13}C-NMR** (150 MHz, DMSO): δ = 163.9, 146.0, 136.8, 134.3, 133.0, 131.7, 130.8, 129.7, 129.0, 128.7, 122.4, 116.2; **HRMS** (ESI^+) calcd for $C_{16}H_{11}BrClN_2O_2$ $[M+H]^+$ 376.9867, found 376.9676.

5. X-ray Crystallographic Data of Compound 3e

Table S1. Crystallography data and structure refinement for **3e (**CCDC 1527208**)**



Empirical formula	$C_{17}H_{13}BrN_2O_2$
Temperature	273 (2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 10.7312 (6) Å alpha = 90 deg. b = 11.0728 (6) Å beta = 90 deg. c = 12.9937 (7) Å gamma = 90 deg.
Volume	1543.97 (15) $Å^3$
Z	19
Calculated density	2.512 g/cm^3
Absorption coefficient	12.385 mm^{-1}
F(000)	1083
Crystal size	0.1 x 0.1x 0.1 cm
Theta range for data collection	2.417 to 26.400 deg
Reflections collected / unique	9239 / 3168 [R(int) = 0.0341]
Data / restraints / parameters	3168 / 0 / 89
Goodness-of-fit on F^2	2.748
Final R indices [I>2sigma(I)]	R1 = 0.1508, wR2 = 0.3735
R indices (all data)	R1 = 0.1658, wR2 = 0.3885

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1. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.* 1978, **43***,* 2923.

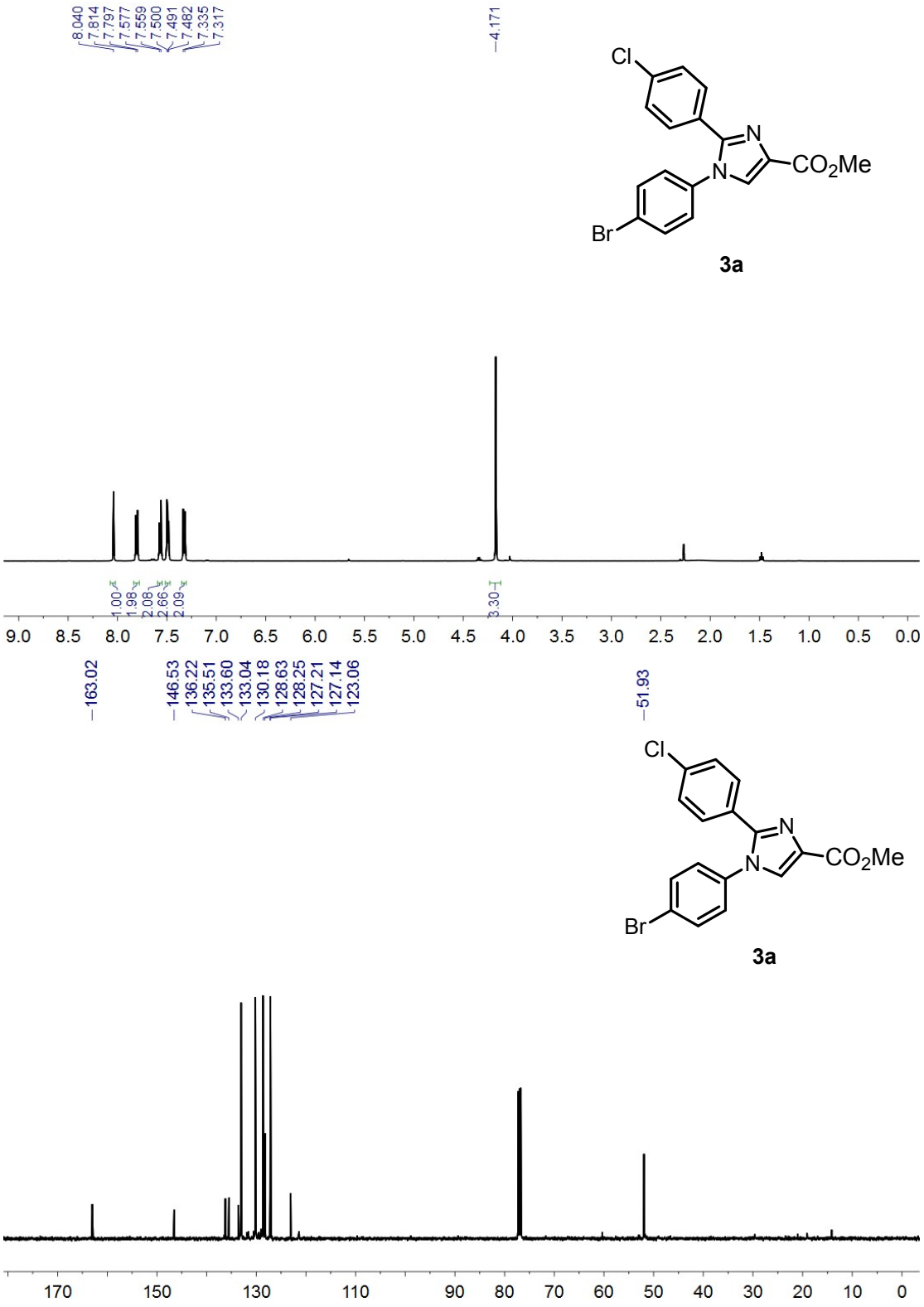
2. S. Kamijo, T. Jin and Y. Yamamoto, *J. Am. Chem. Soc.* 2001, **123**, 9453.

3. (a) T. Da, A. Kayet, R. Mishraa and V.K. Singh, *Chem. Commun.* 2016, **52**, 11231. (b) S. Cabrera, R. Gómez Arrayás and J. C. Carretero, *J. Am. Chem. Soc.* 2005, **127**, 16394. (c) C. Nájera, M. de Garcia Retamosa and J. M. Sansano, *Org. Lett.* 2007, **9**, 4025.

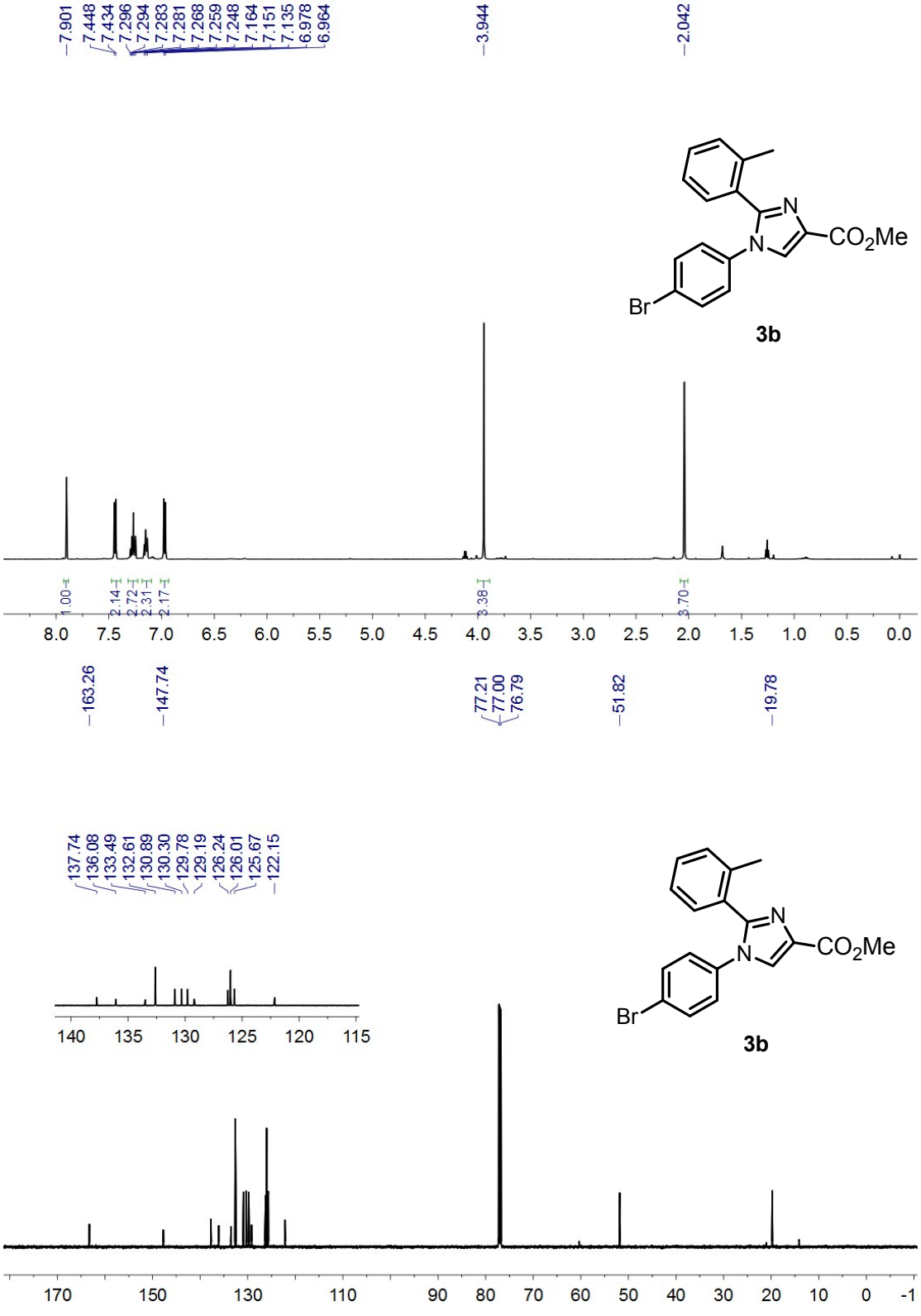
4. B. Asproni, G. Talani, F. Busonero, A. Pau, S. Sanna, R. Cerri, M.P. Mascia, E. Sanna and G. Biggio, *J. Med. Chem.* 2005, **48**, 2638.

6. ^{1}H and ^{13}C-NMR spectra copies

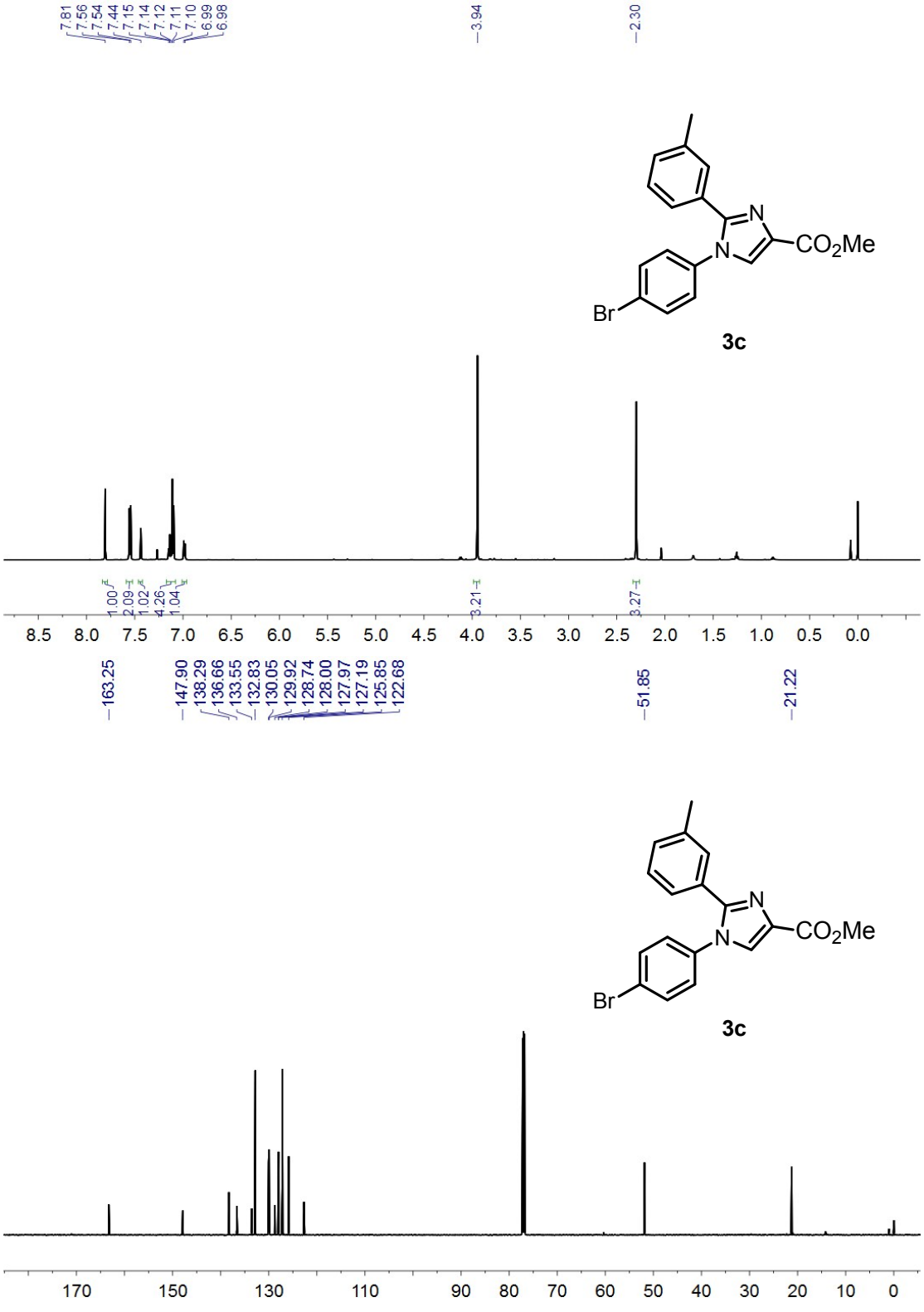
3a ^{1}H-NMR (500 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 125 MHz)



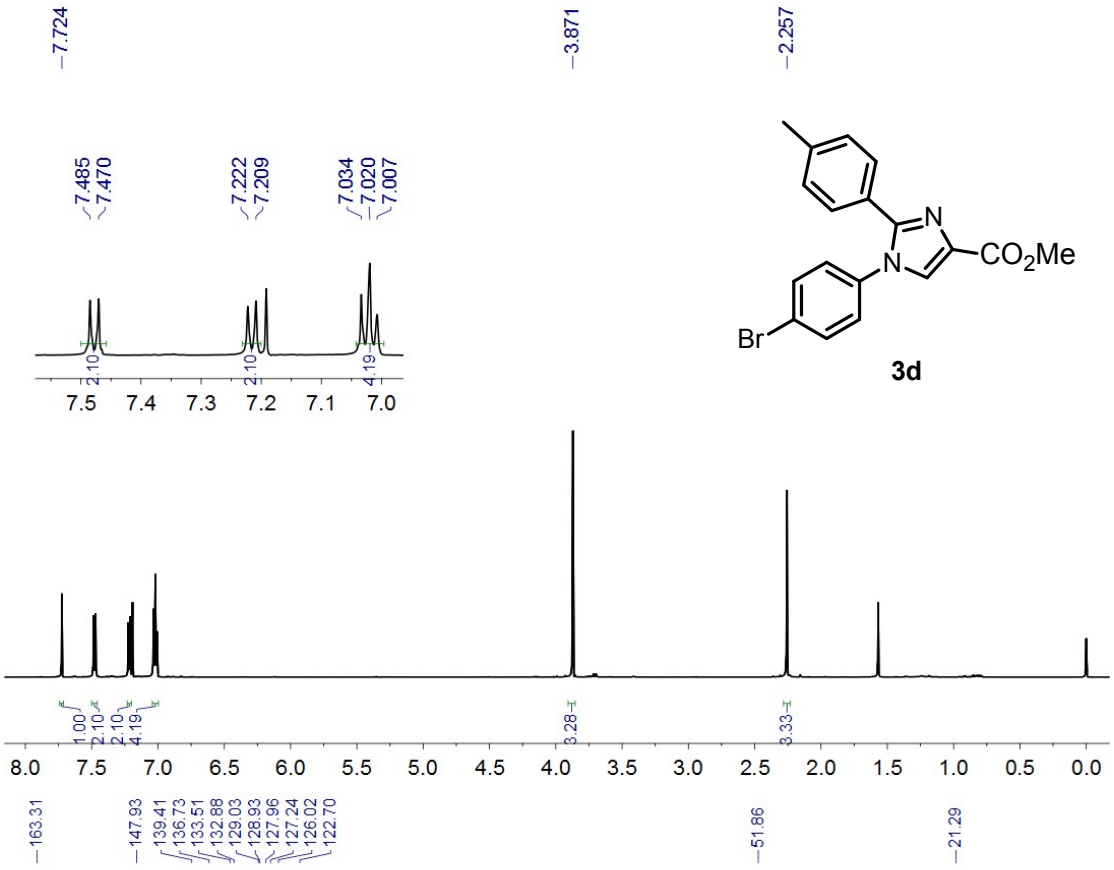
3b **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

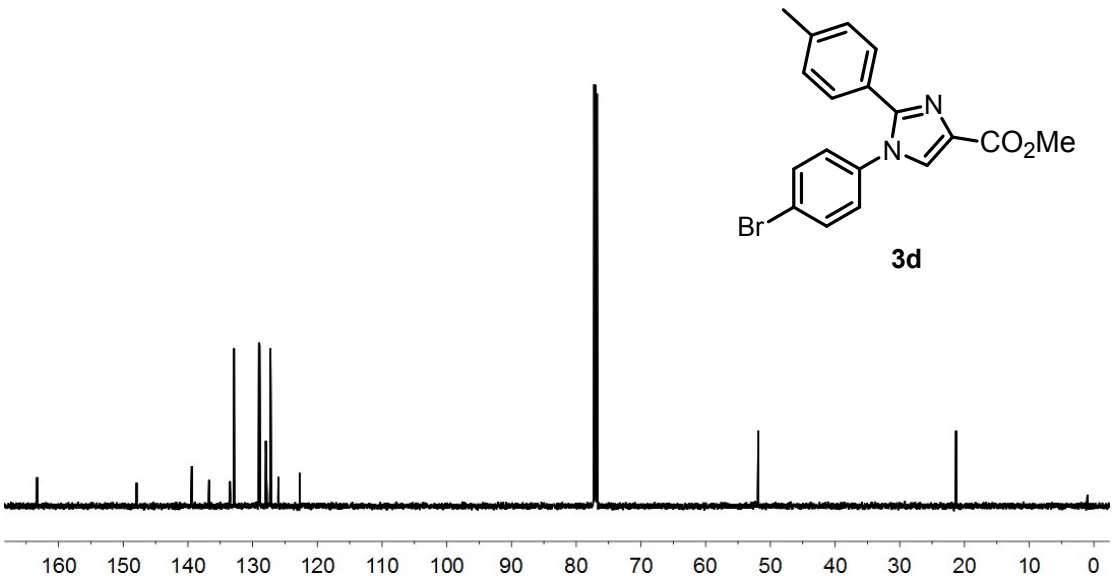


3c **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

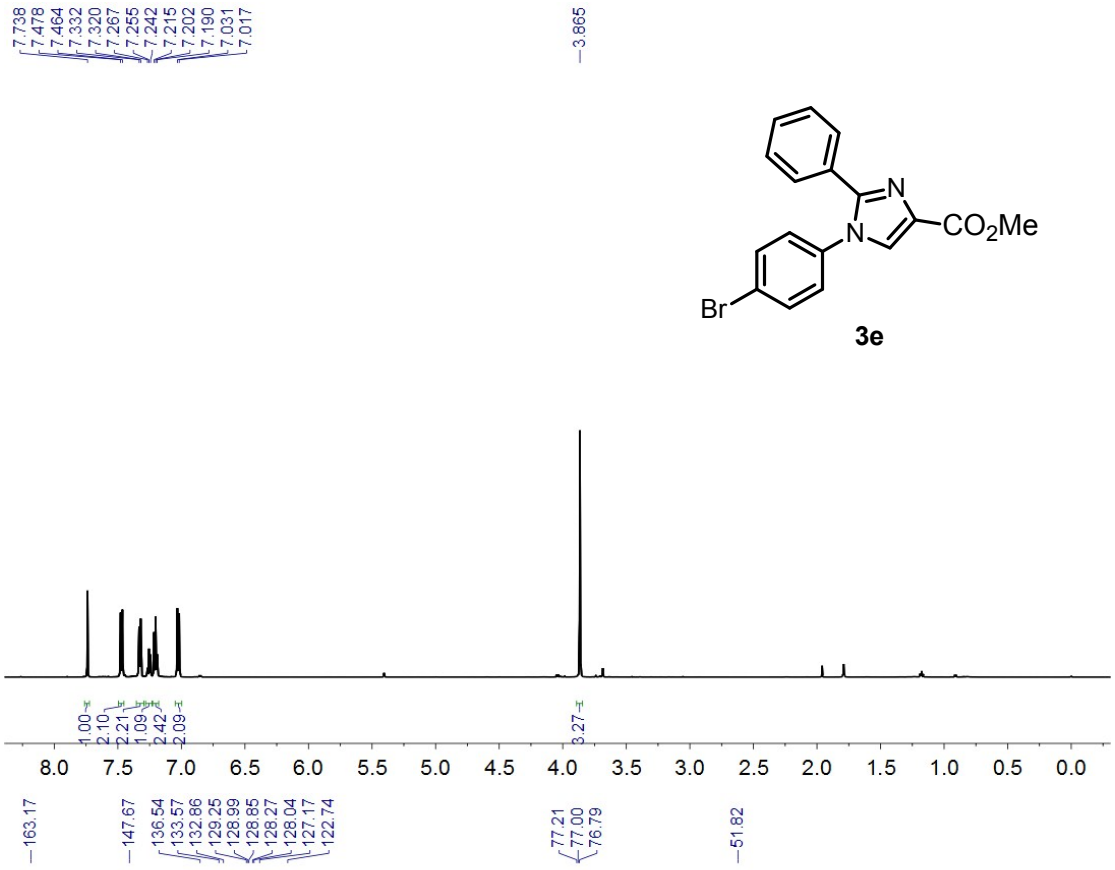


3d **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

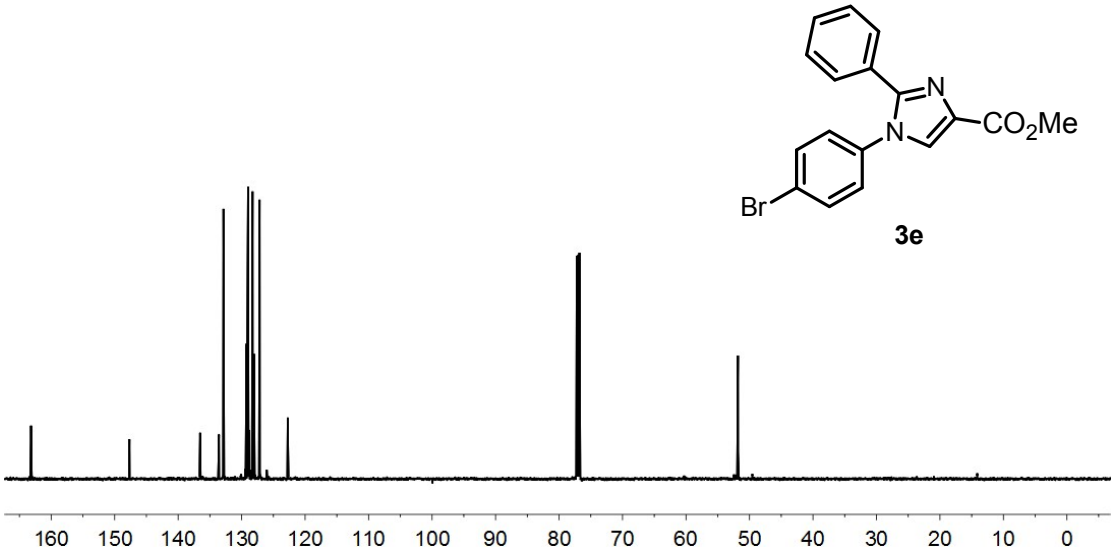




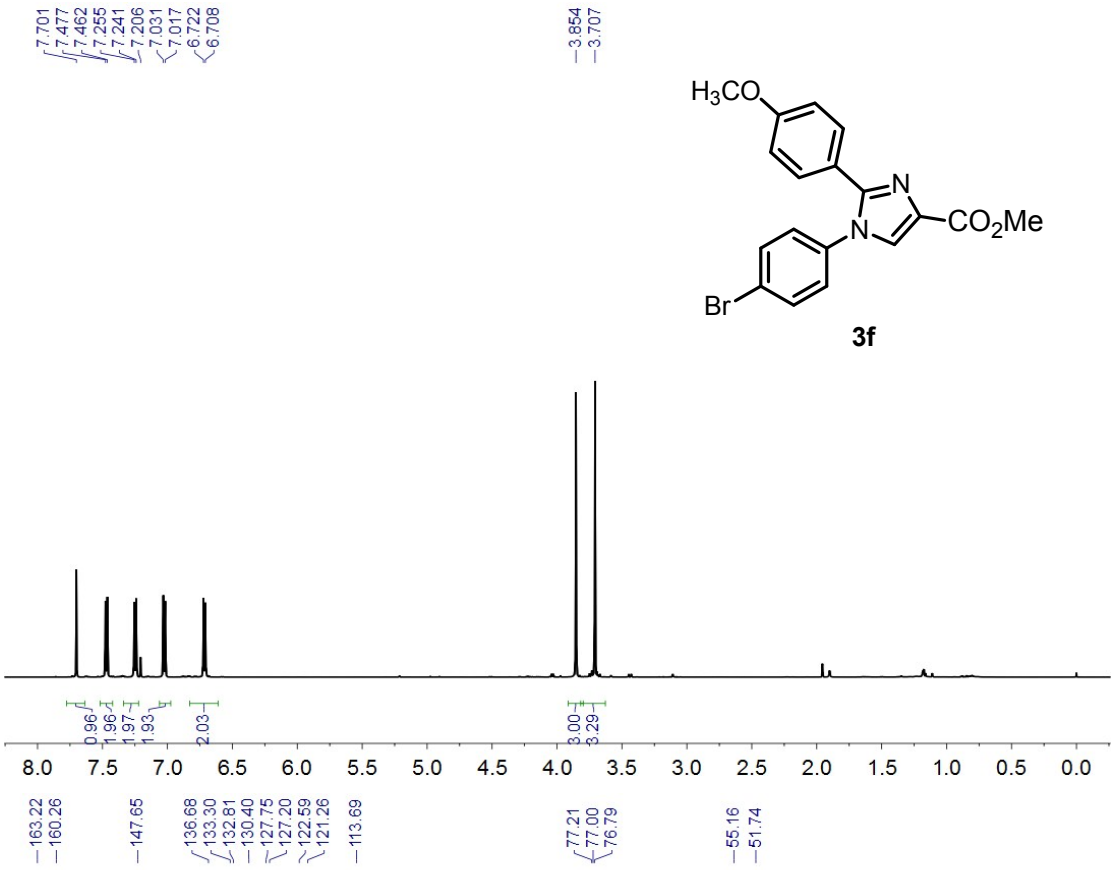
3e ^{1}H-NMR (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



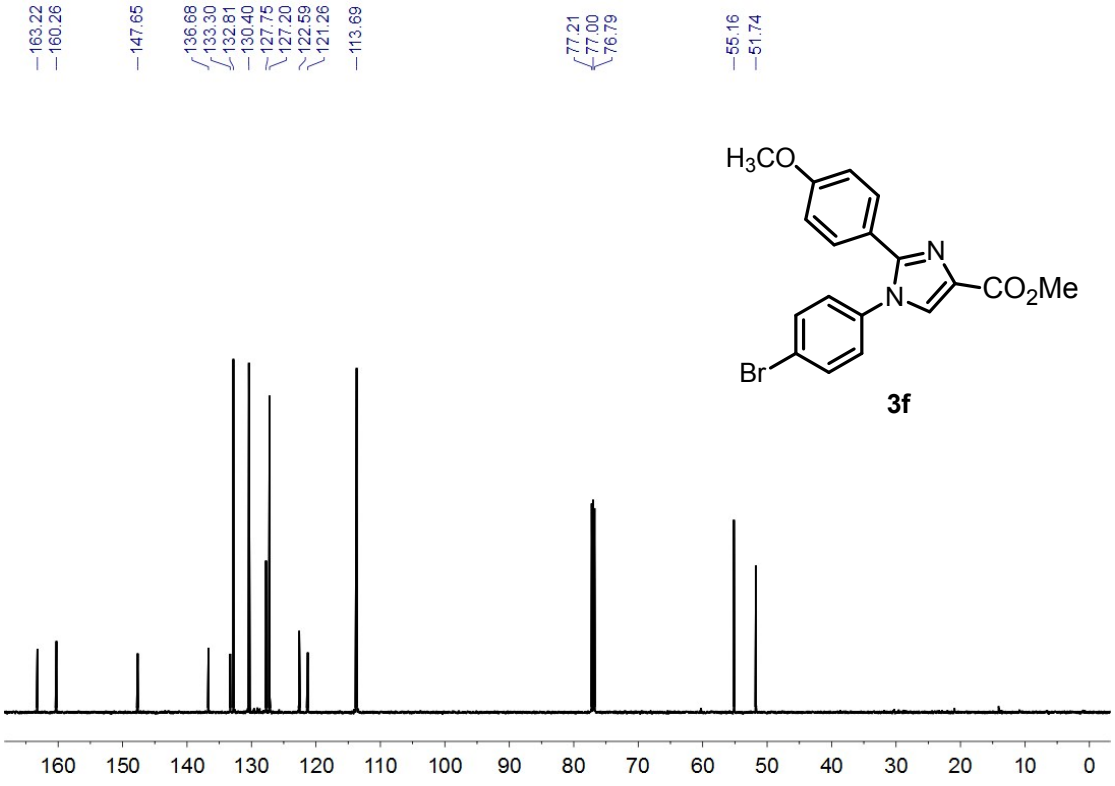
3e



3f **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

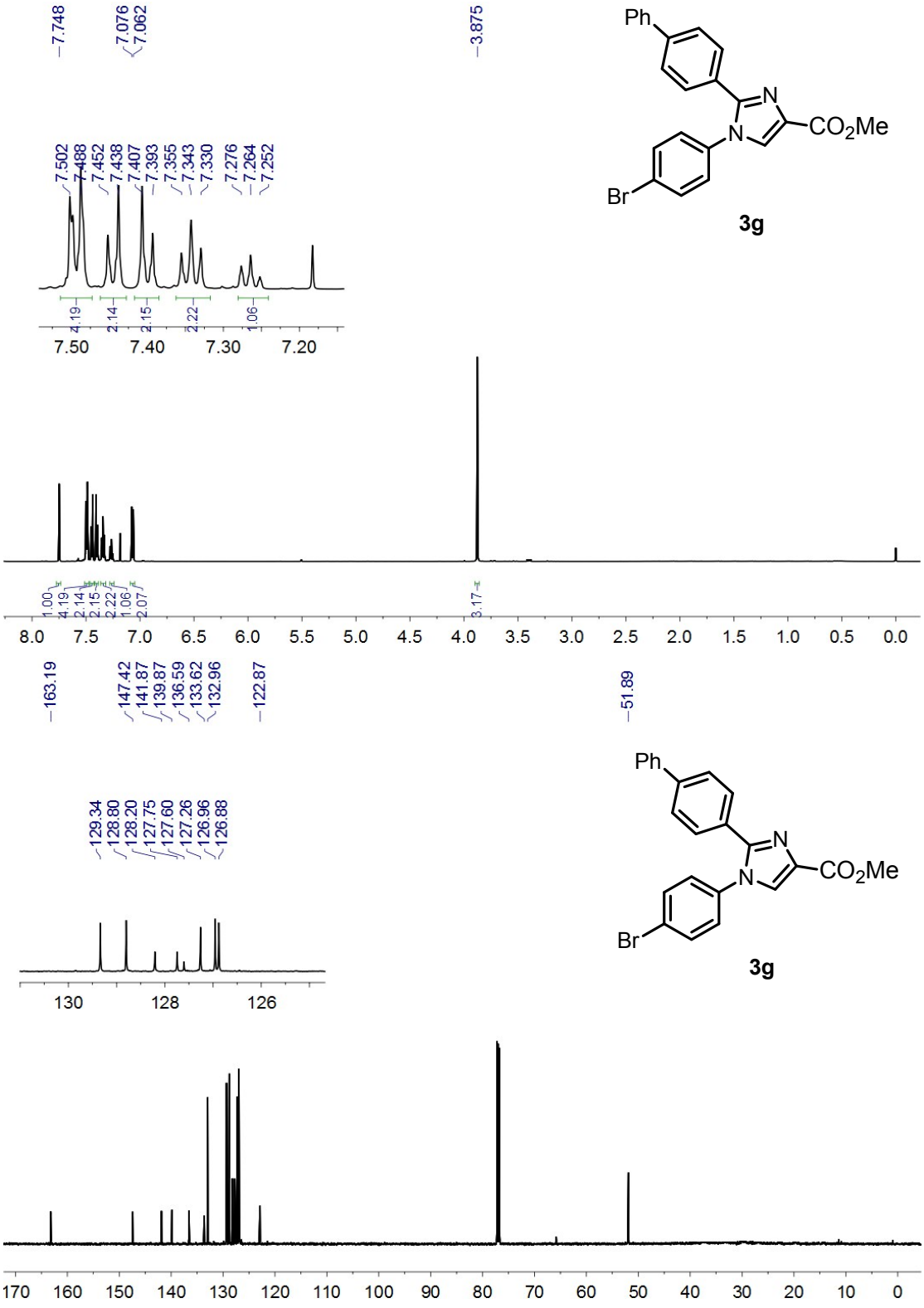


3f

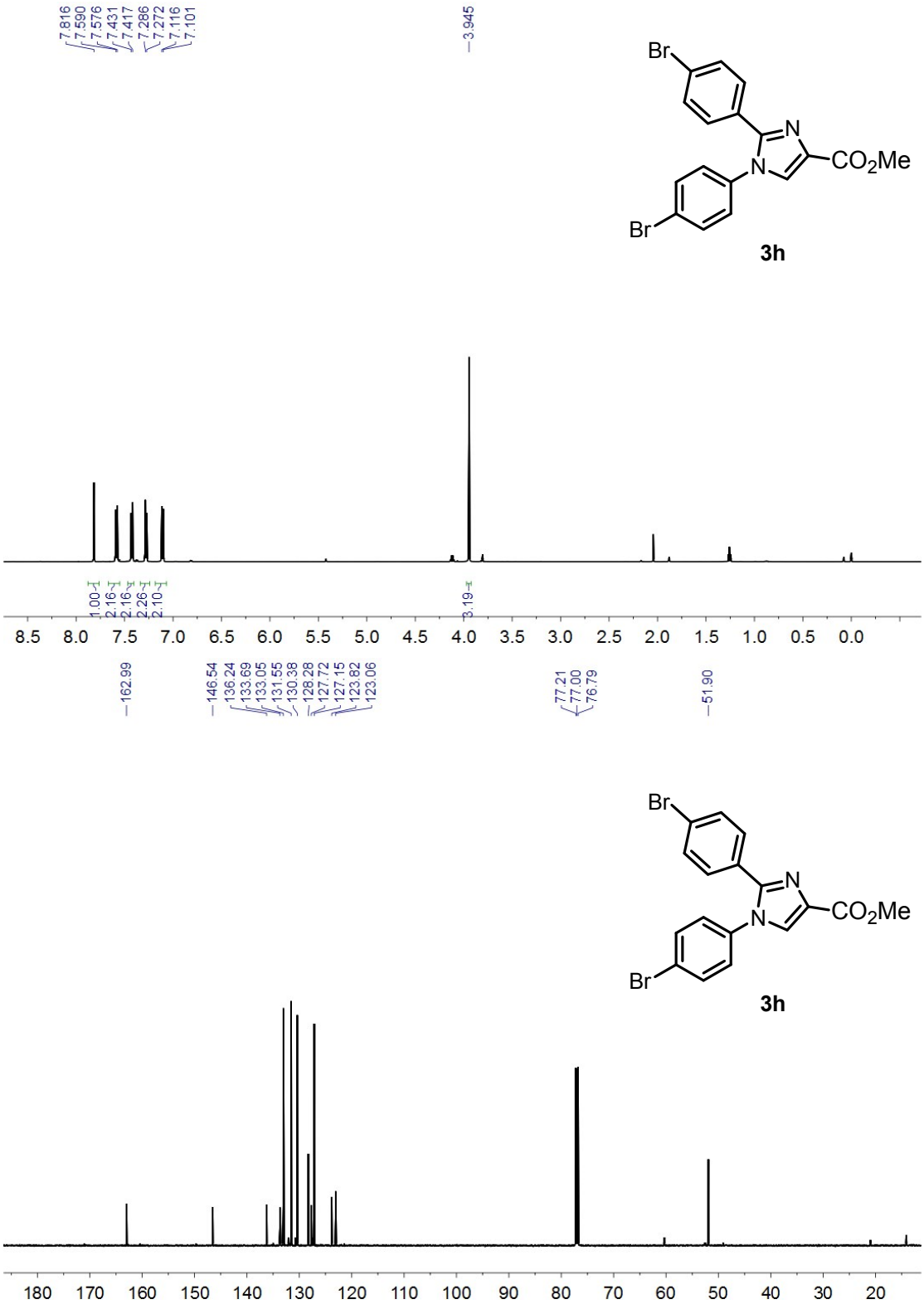


3f

3g **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

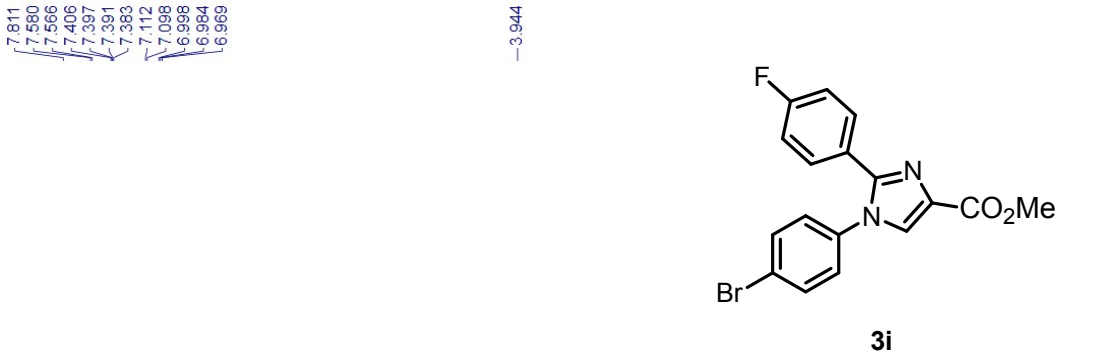


3h **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

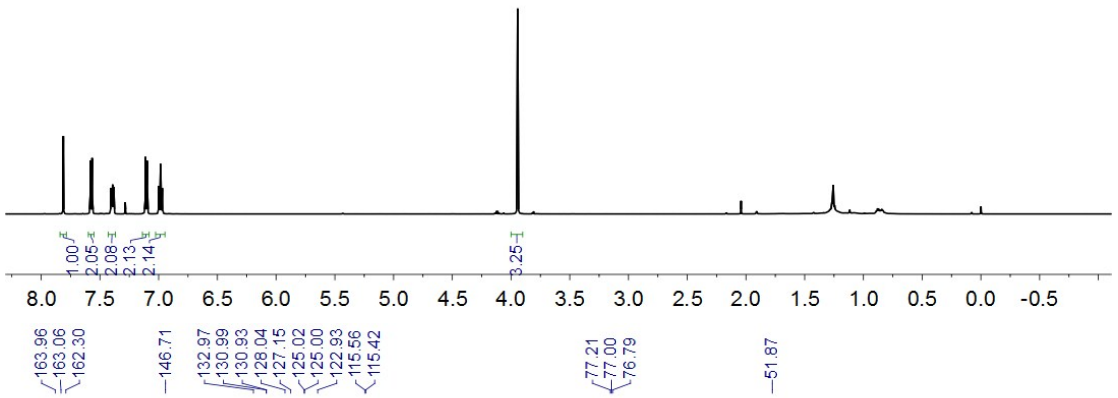


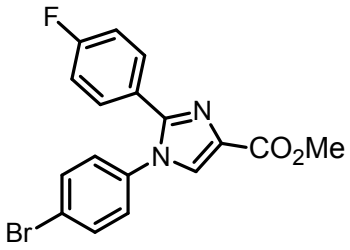
3h

3i **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

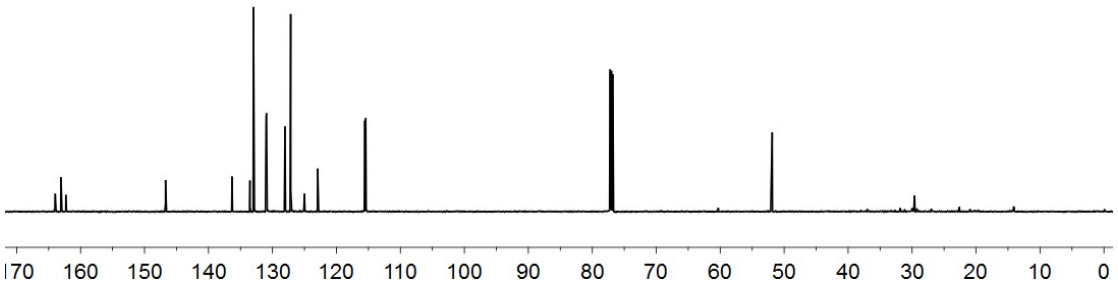


3i

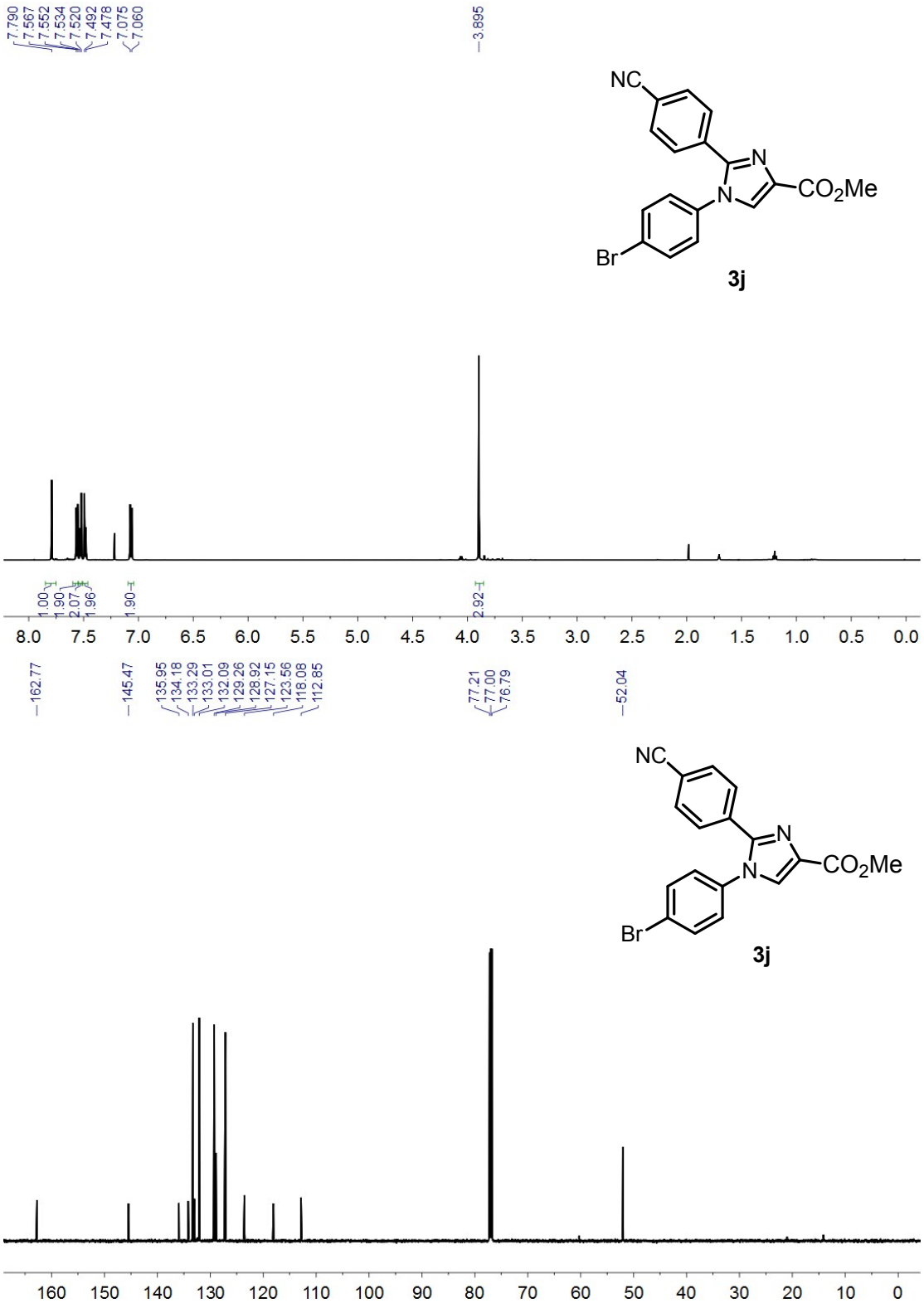




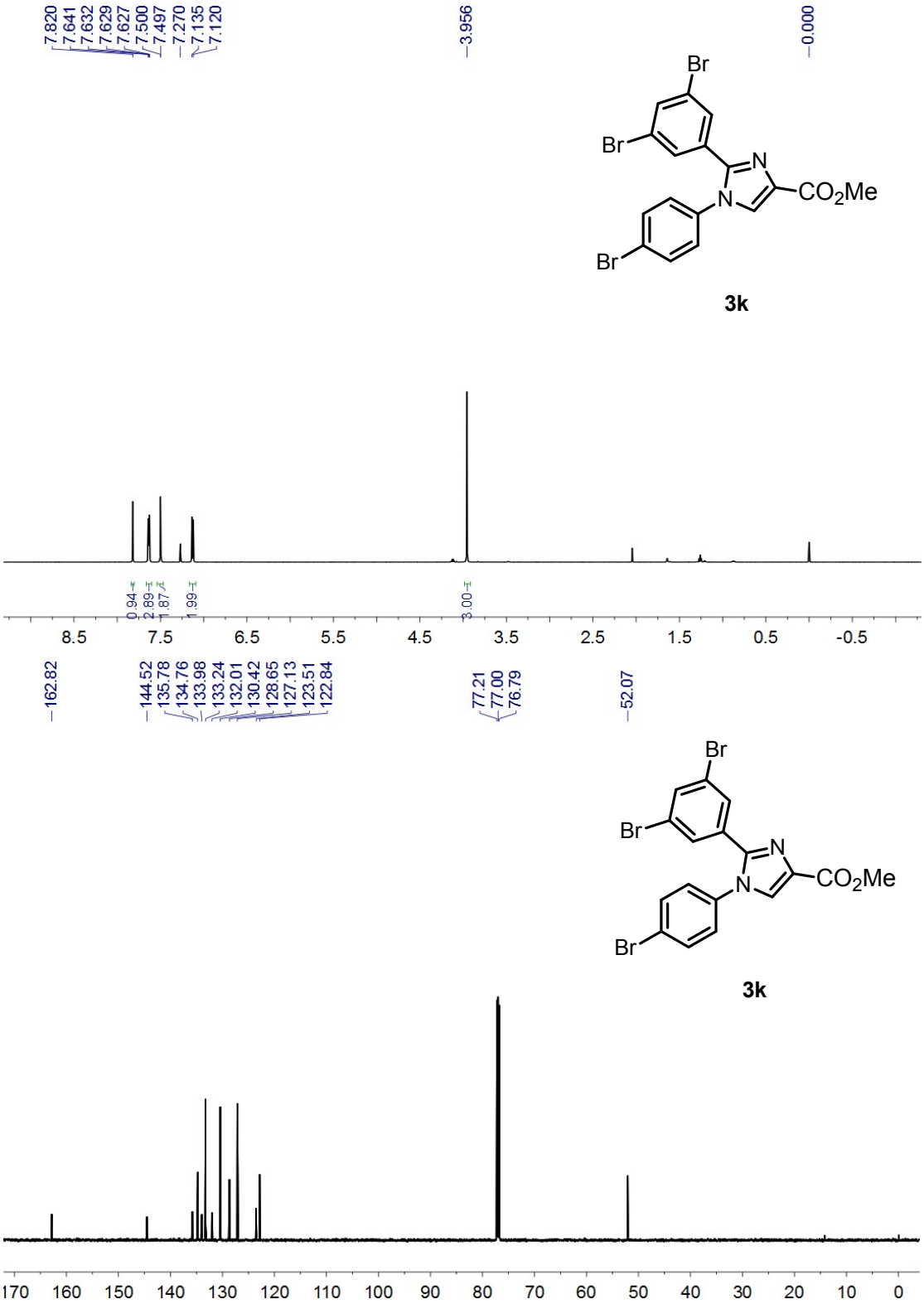
3i



3j **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

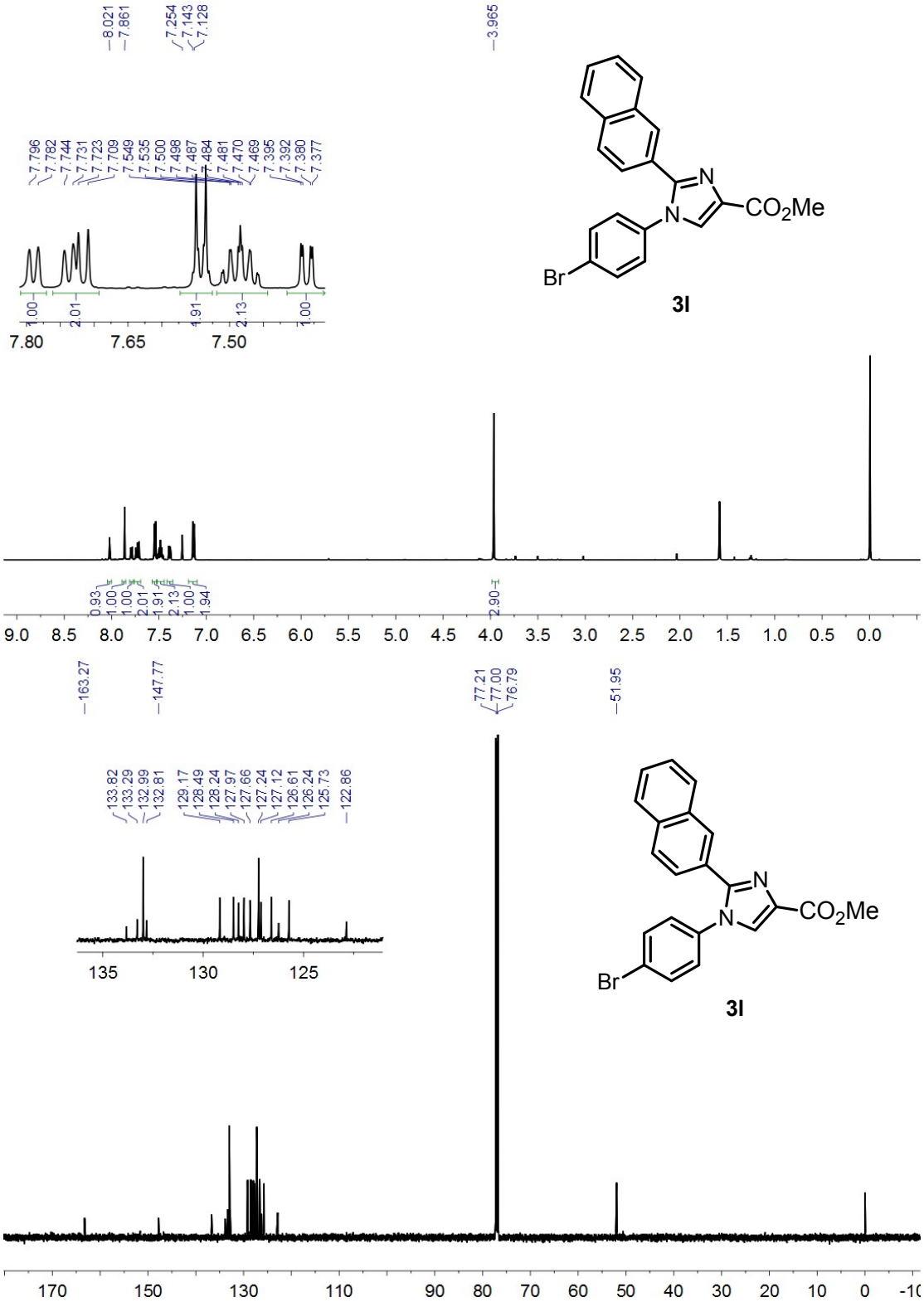


3k **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

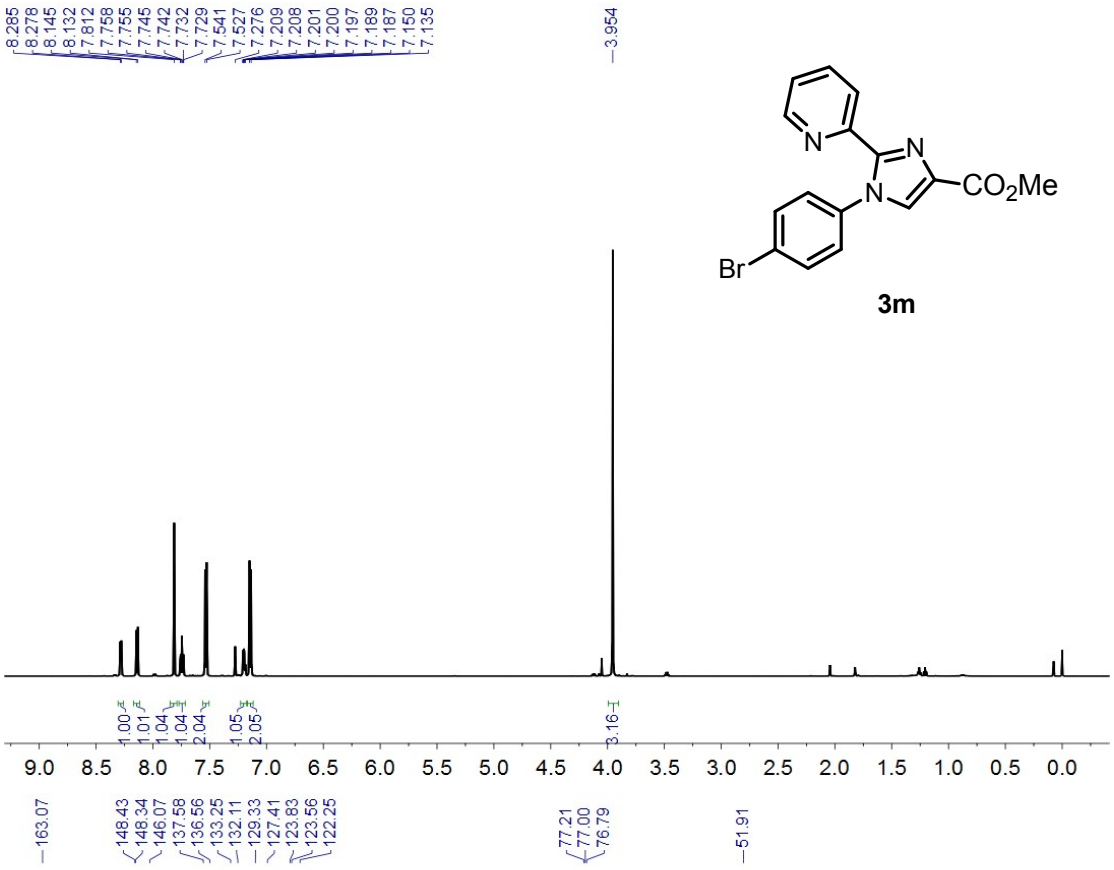


3k

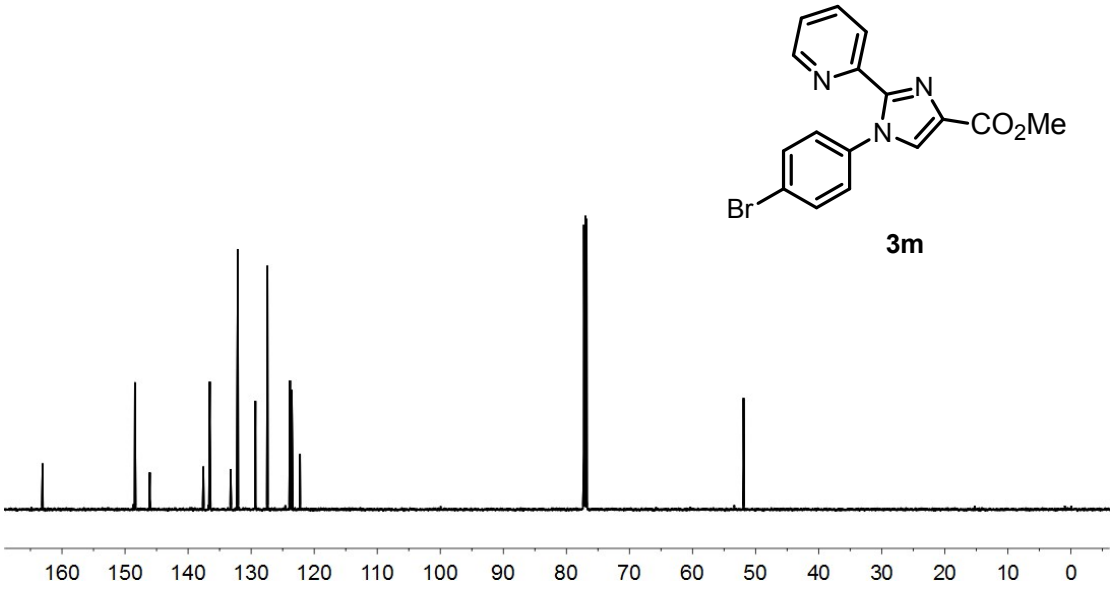
3l **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



3m **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

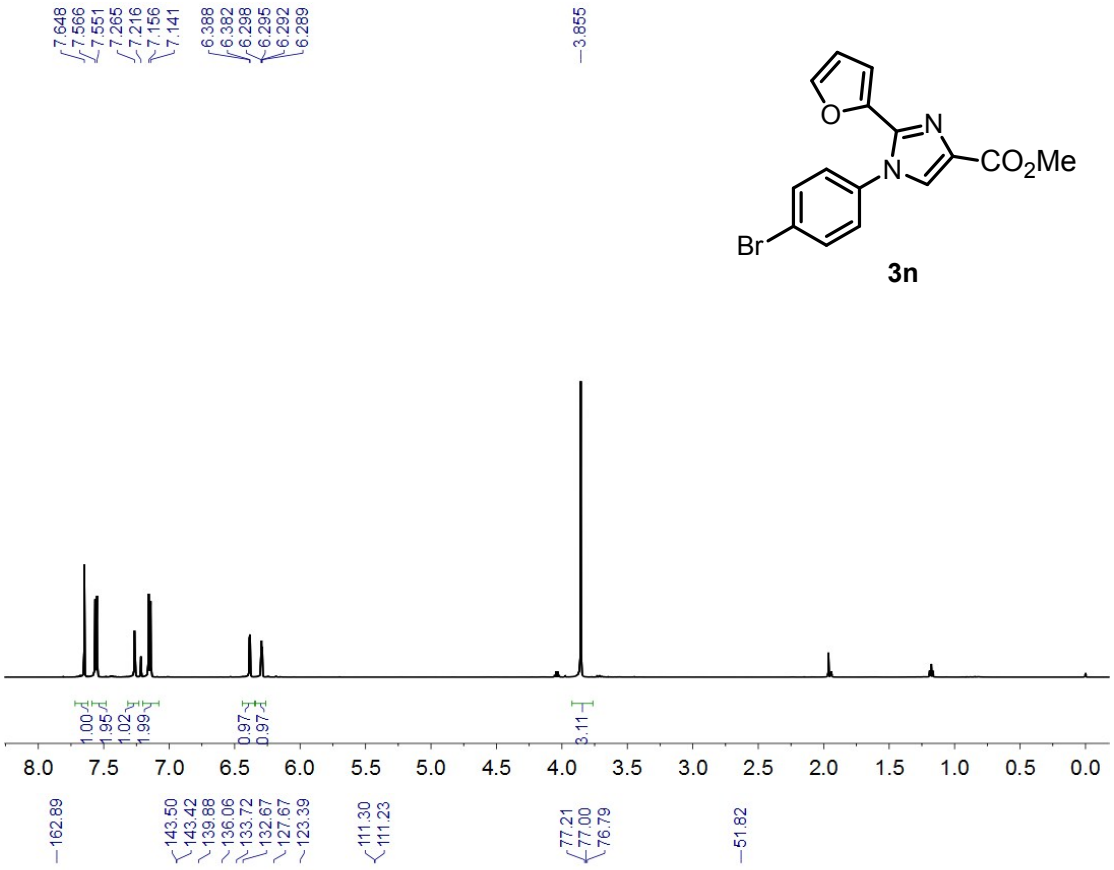


3m

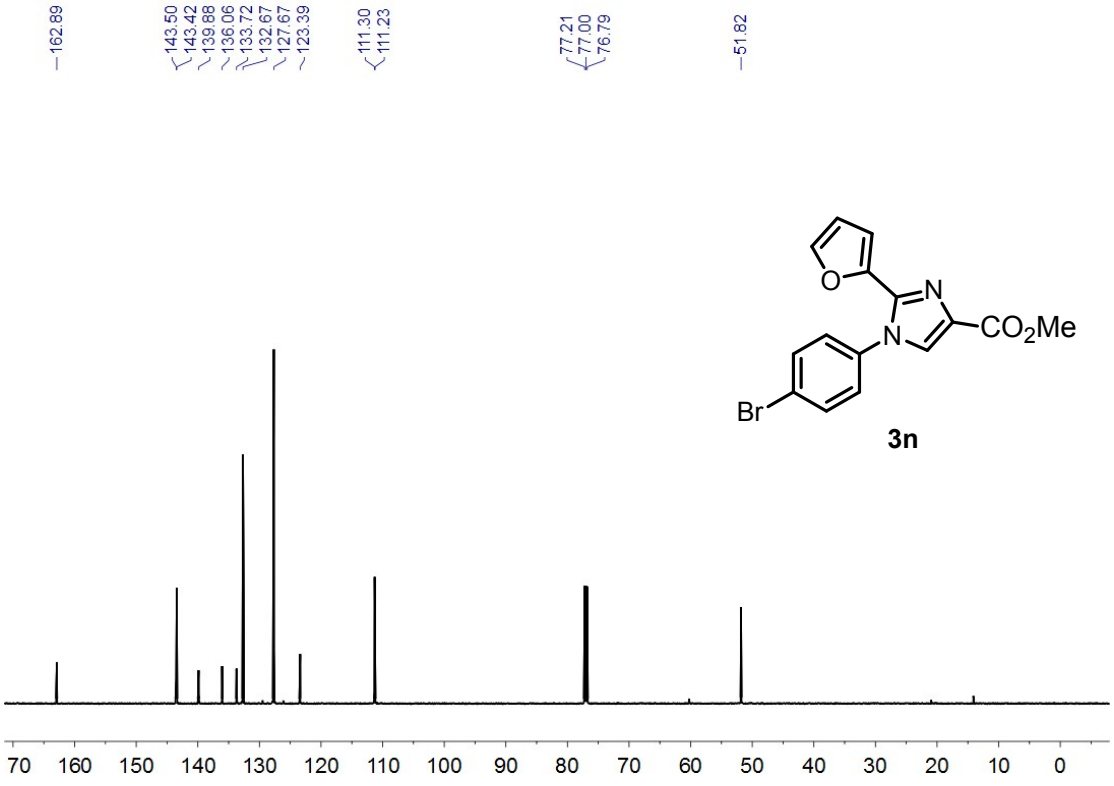


3m

3n **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

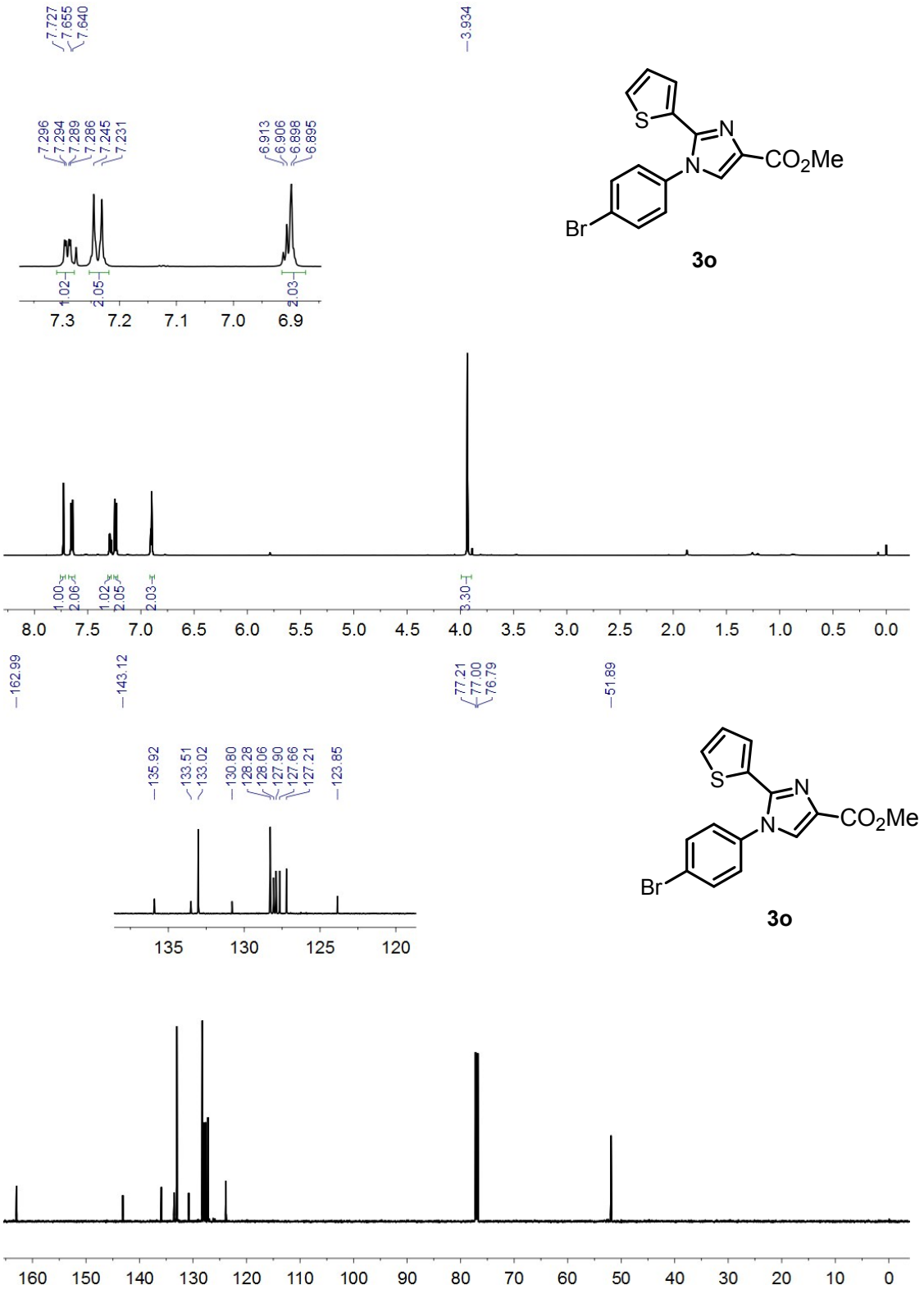


3n

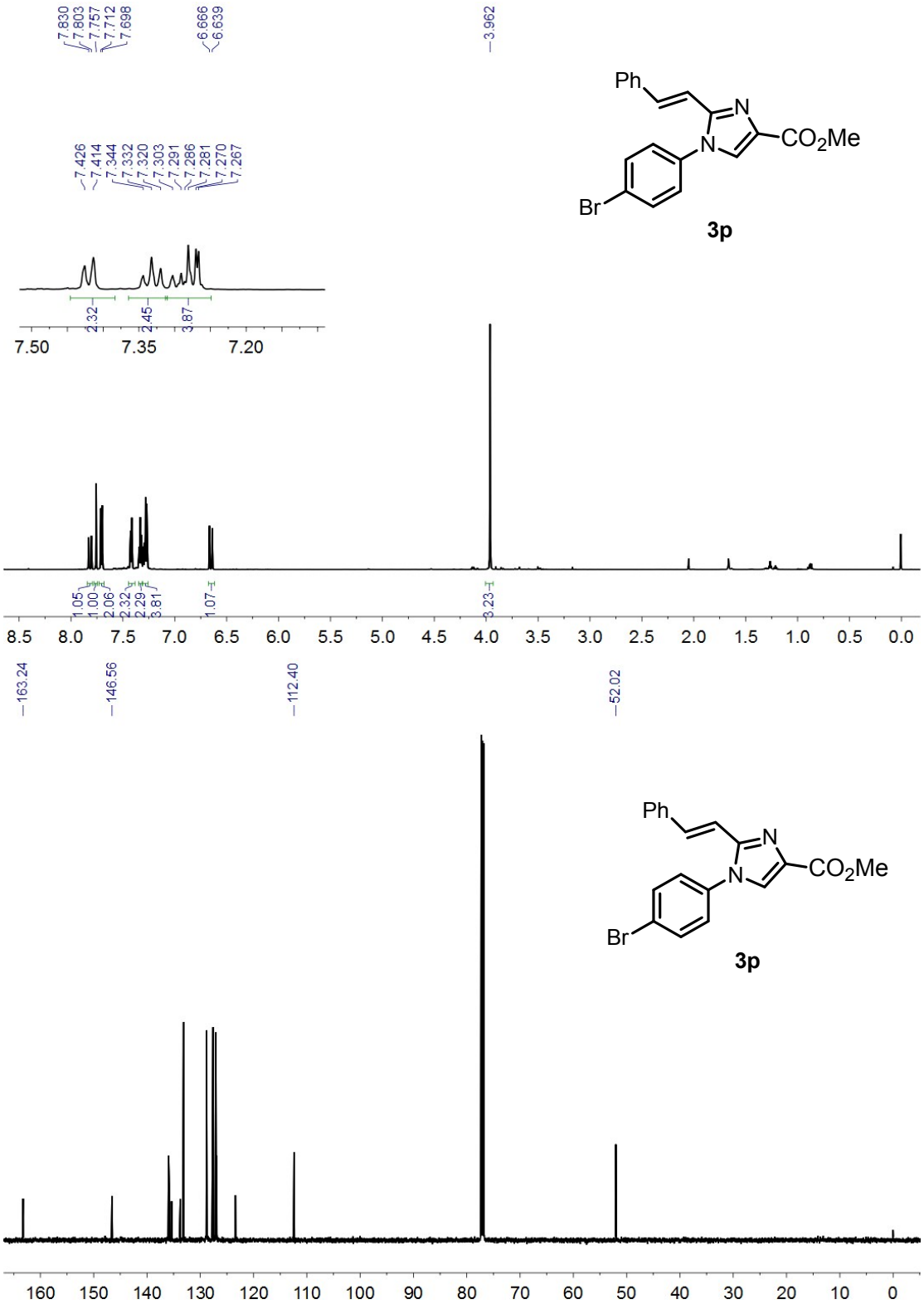


3n

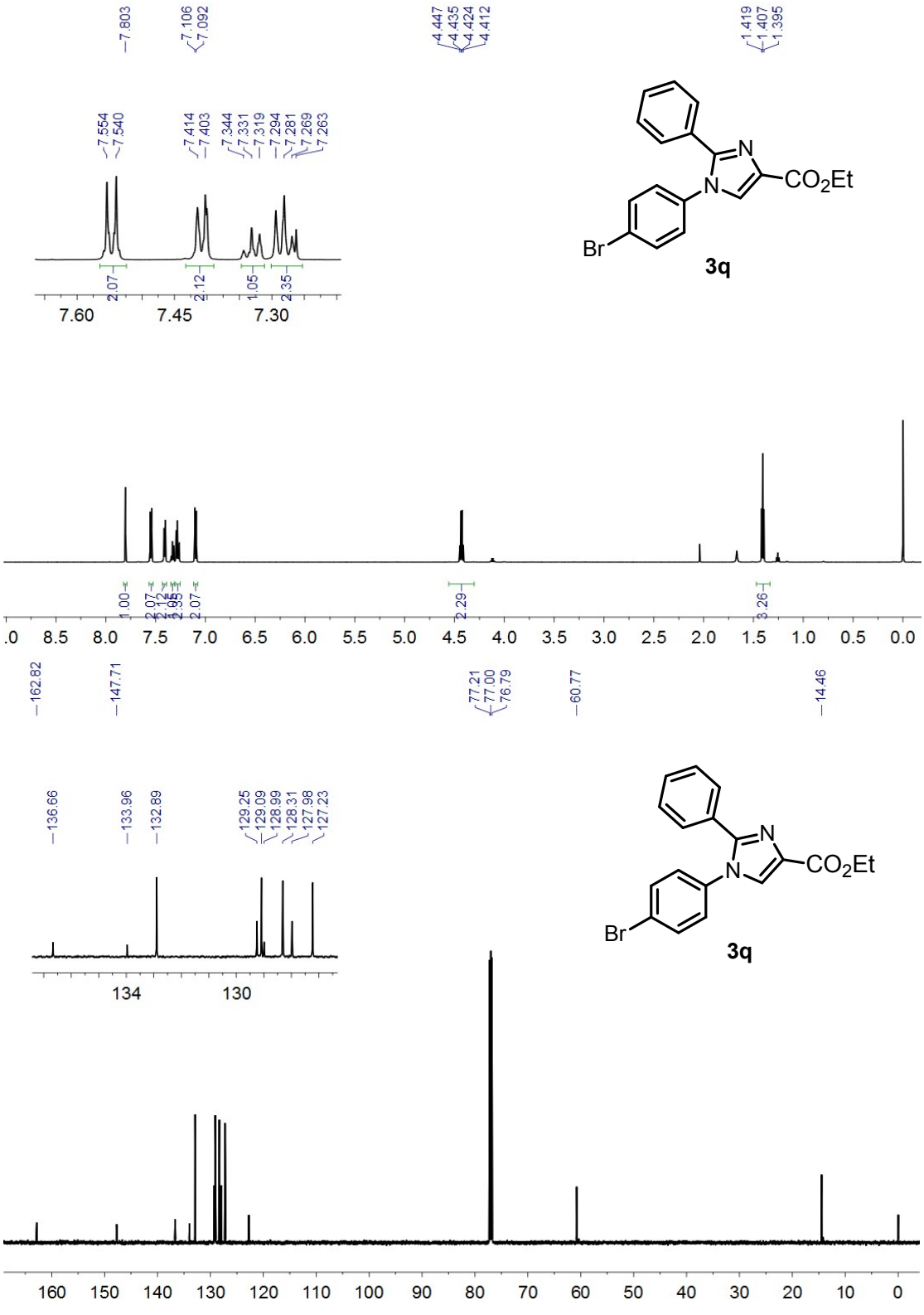
3o **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



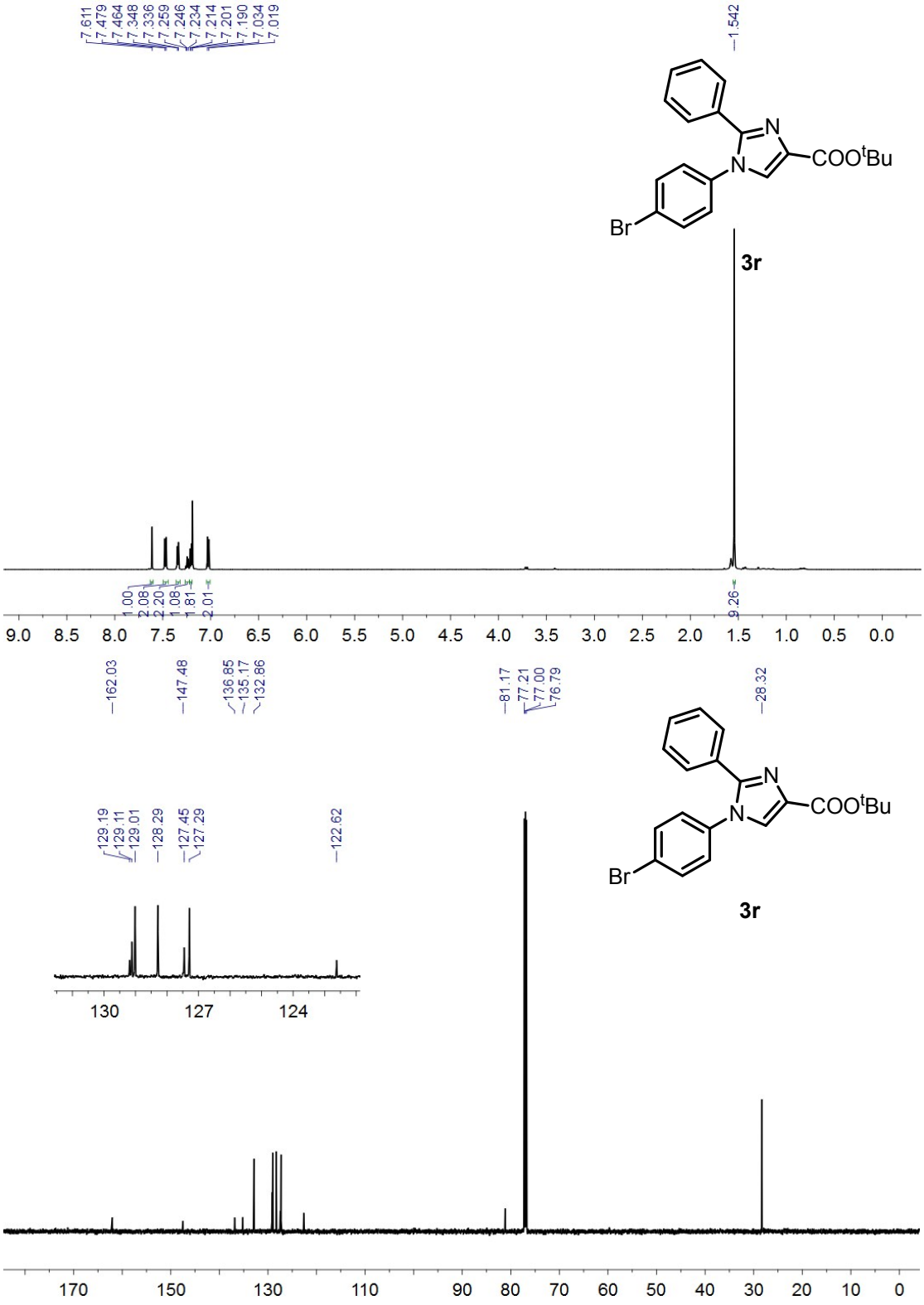
3p **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



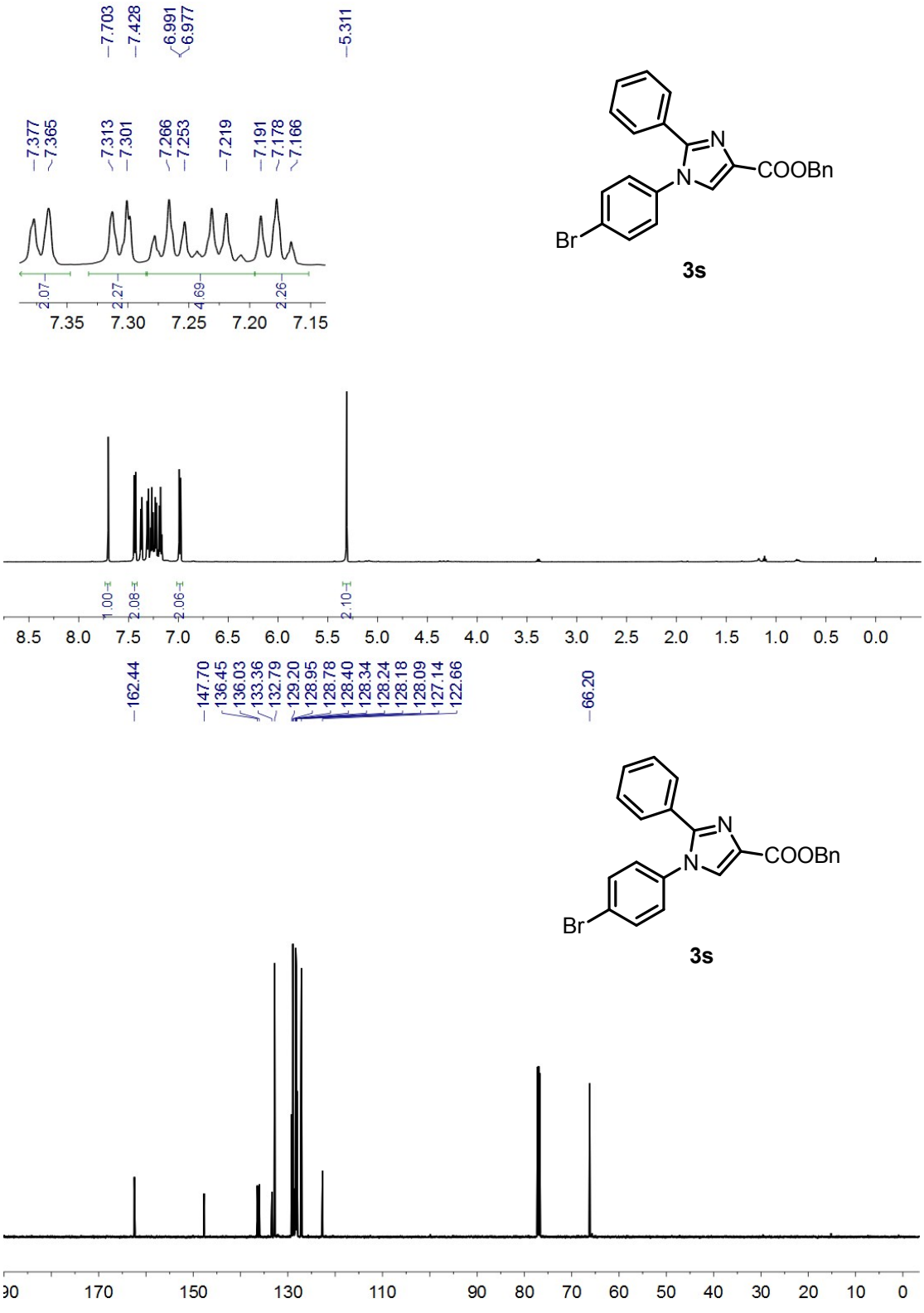
3q **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



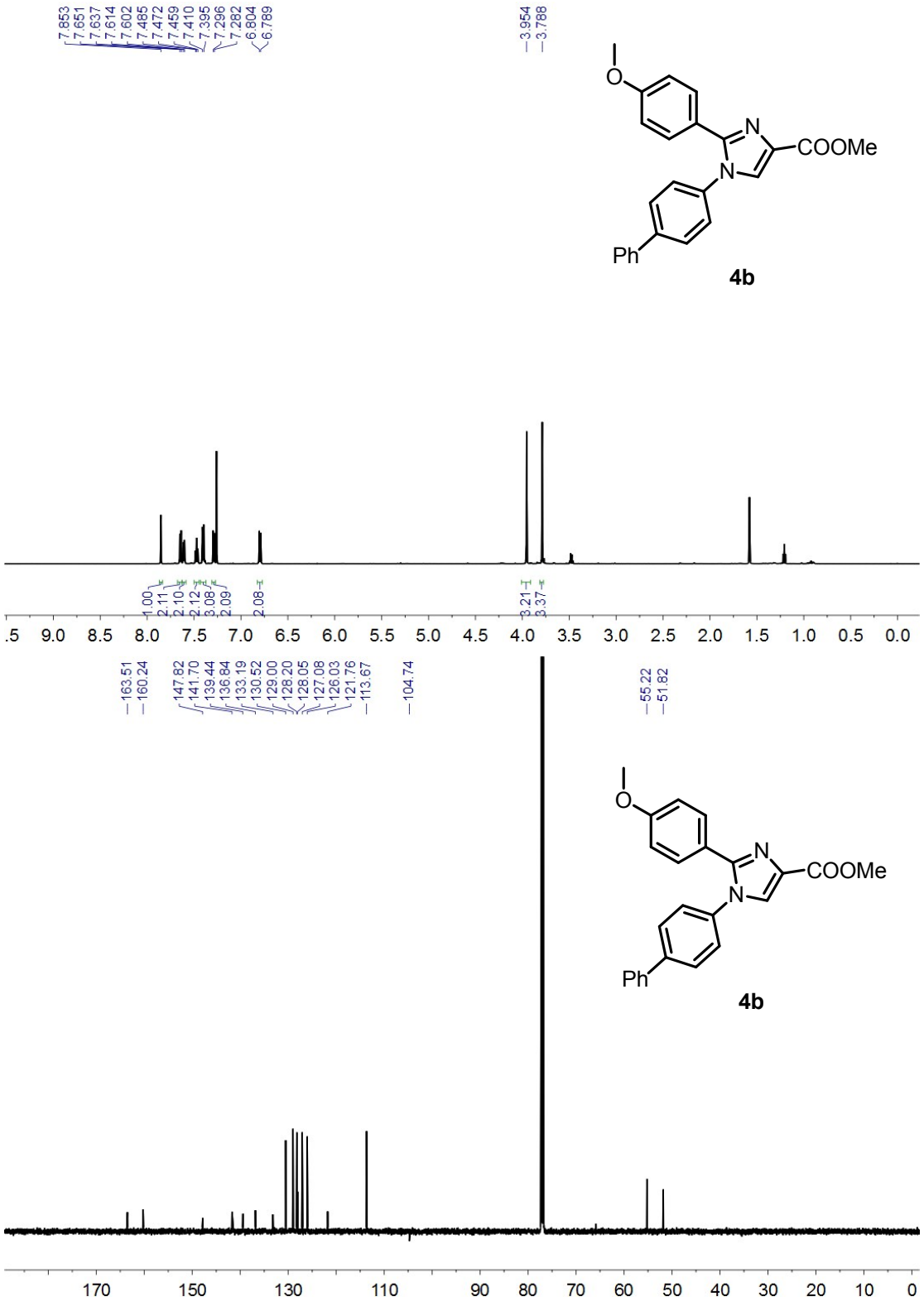
3r **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



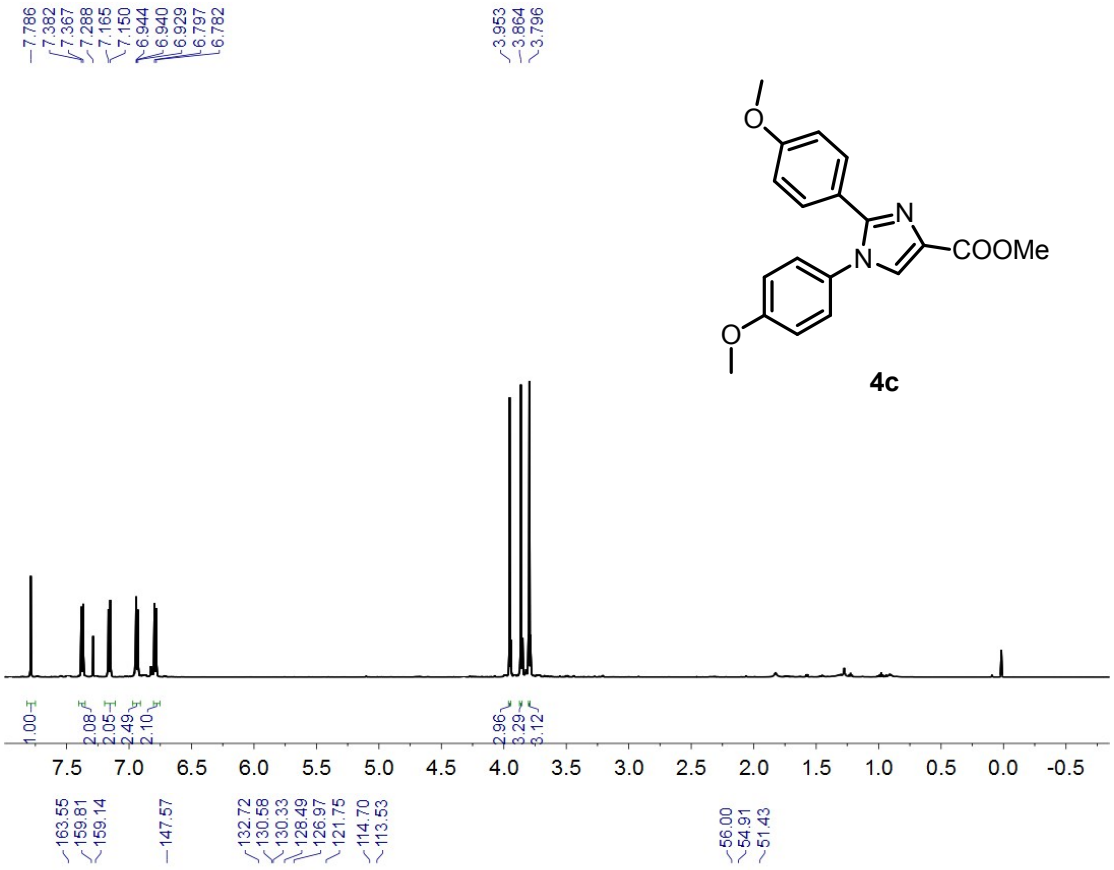
3s **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

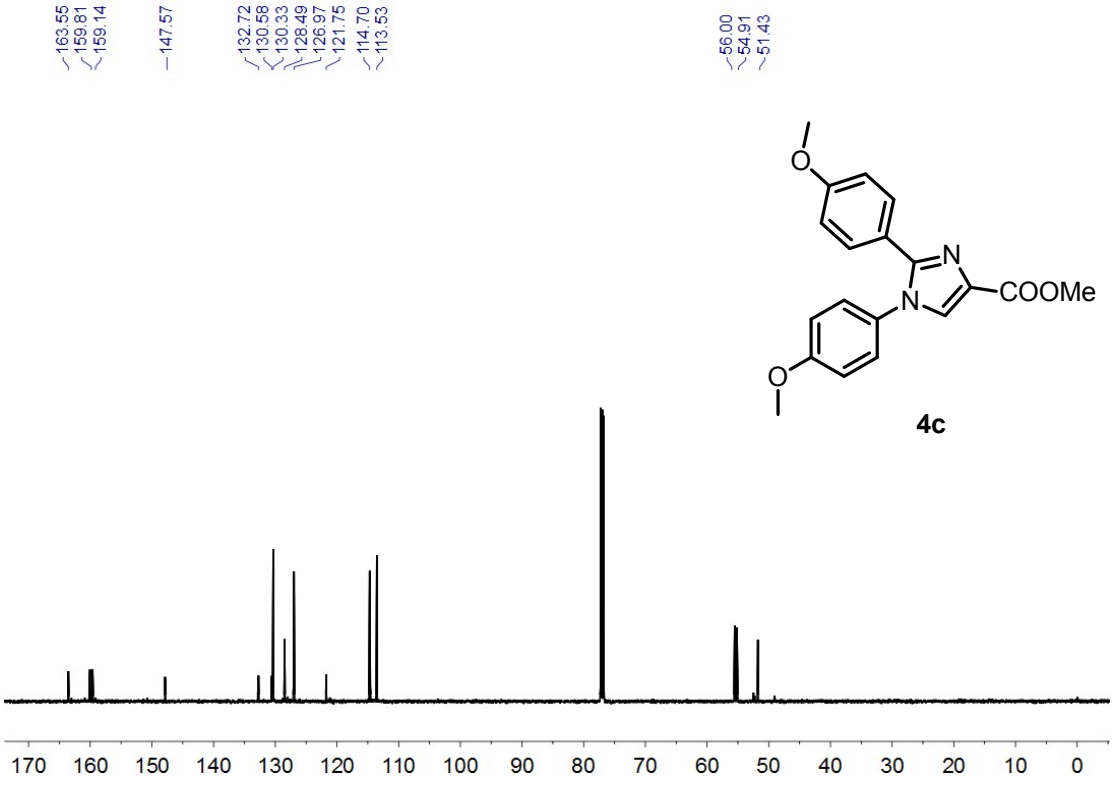


4b **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

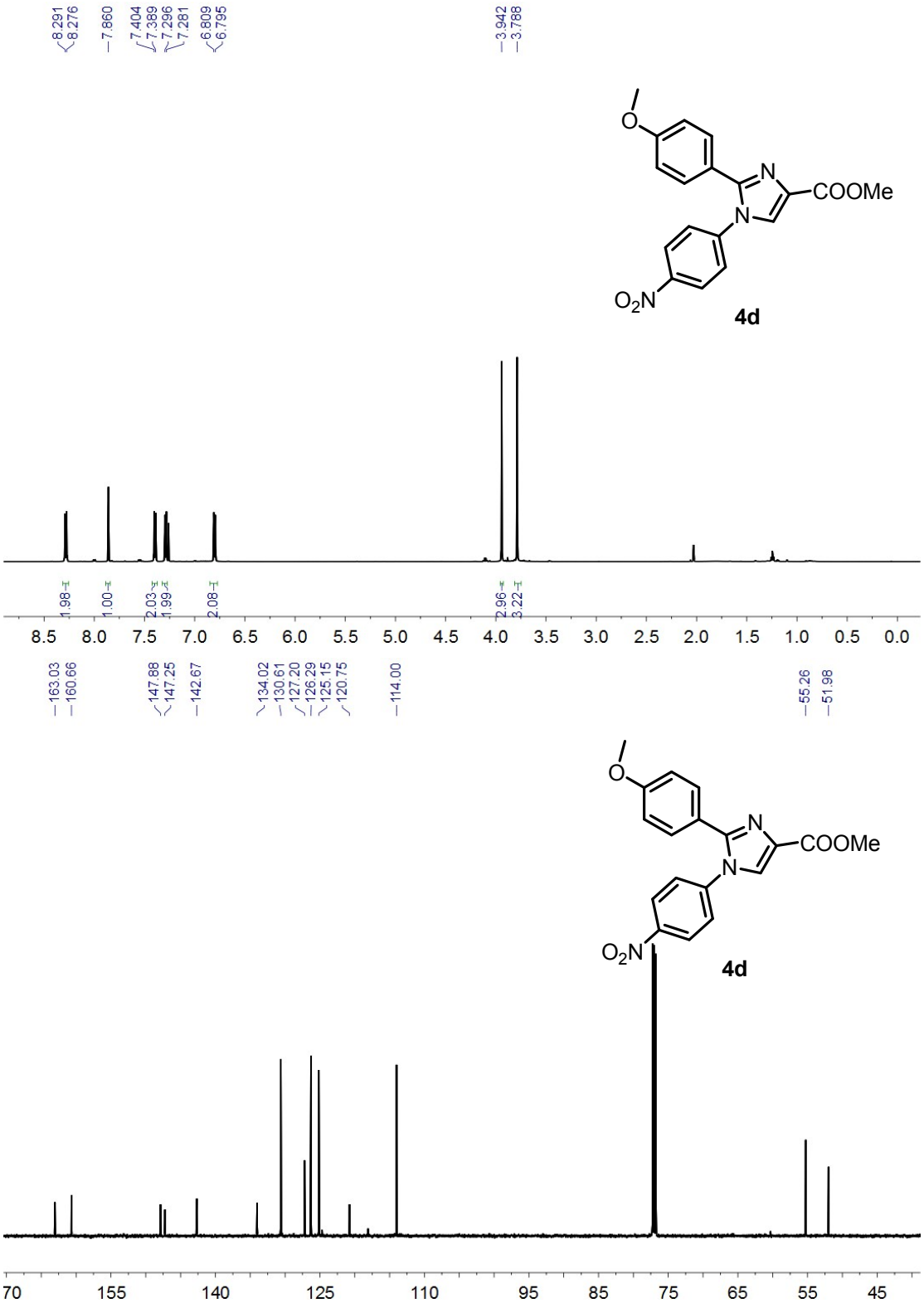


4c **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

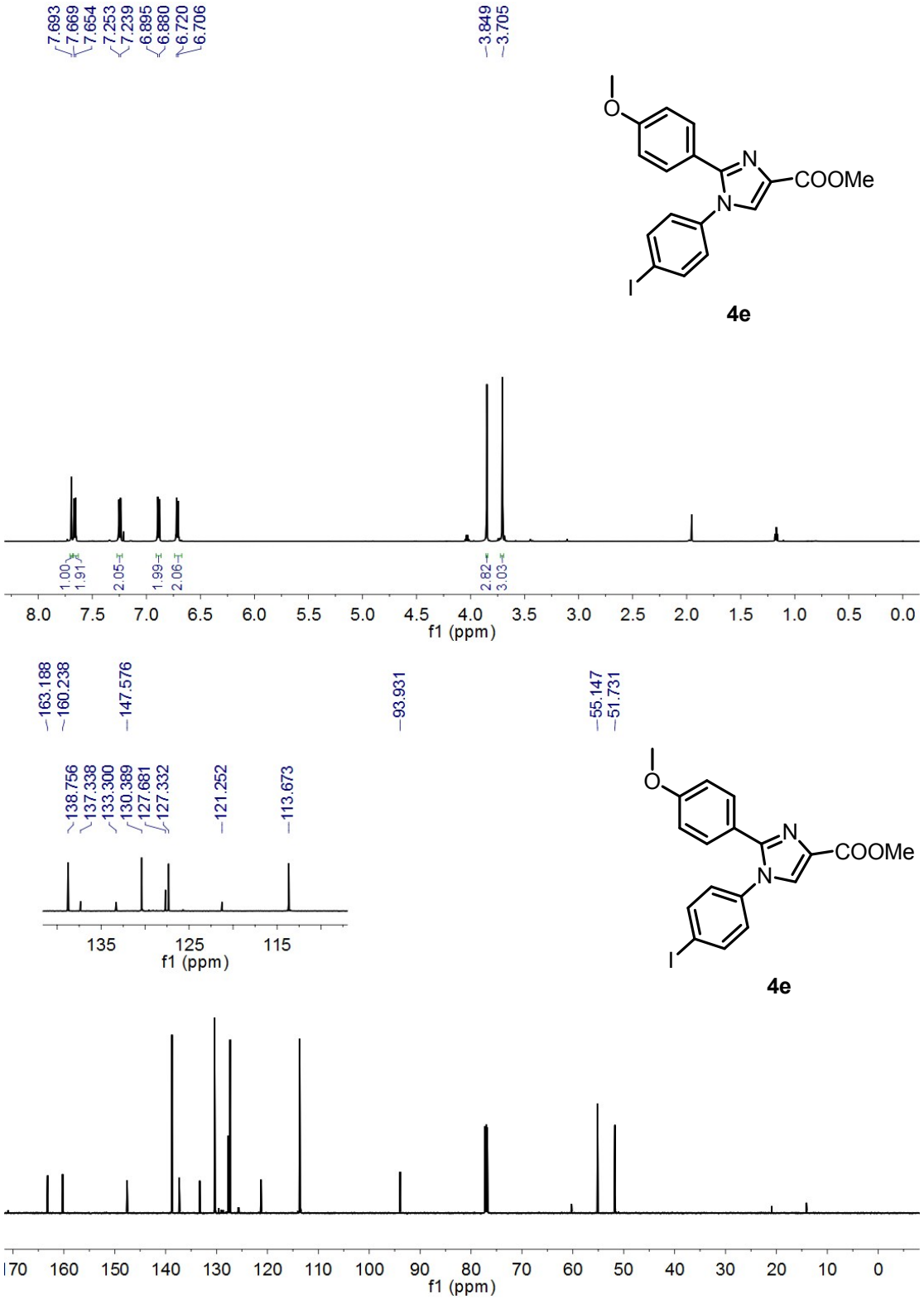




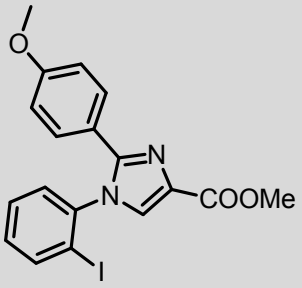
4d ^{1}H-NMR (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



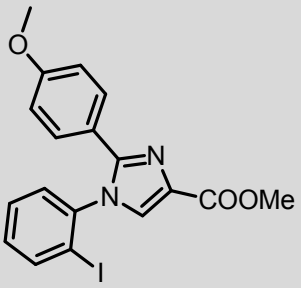
4e ^{1}H-NMR (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



4f **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

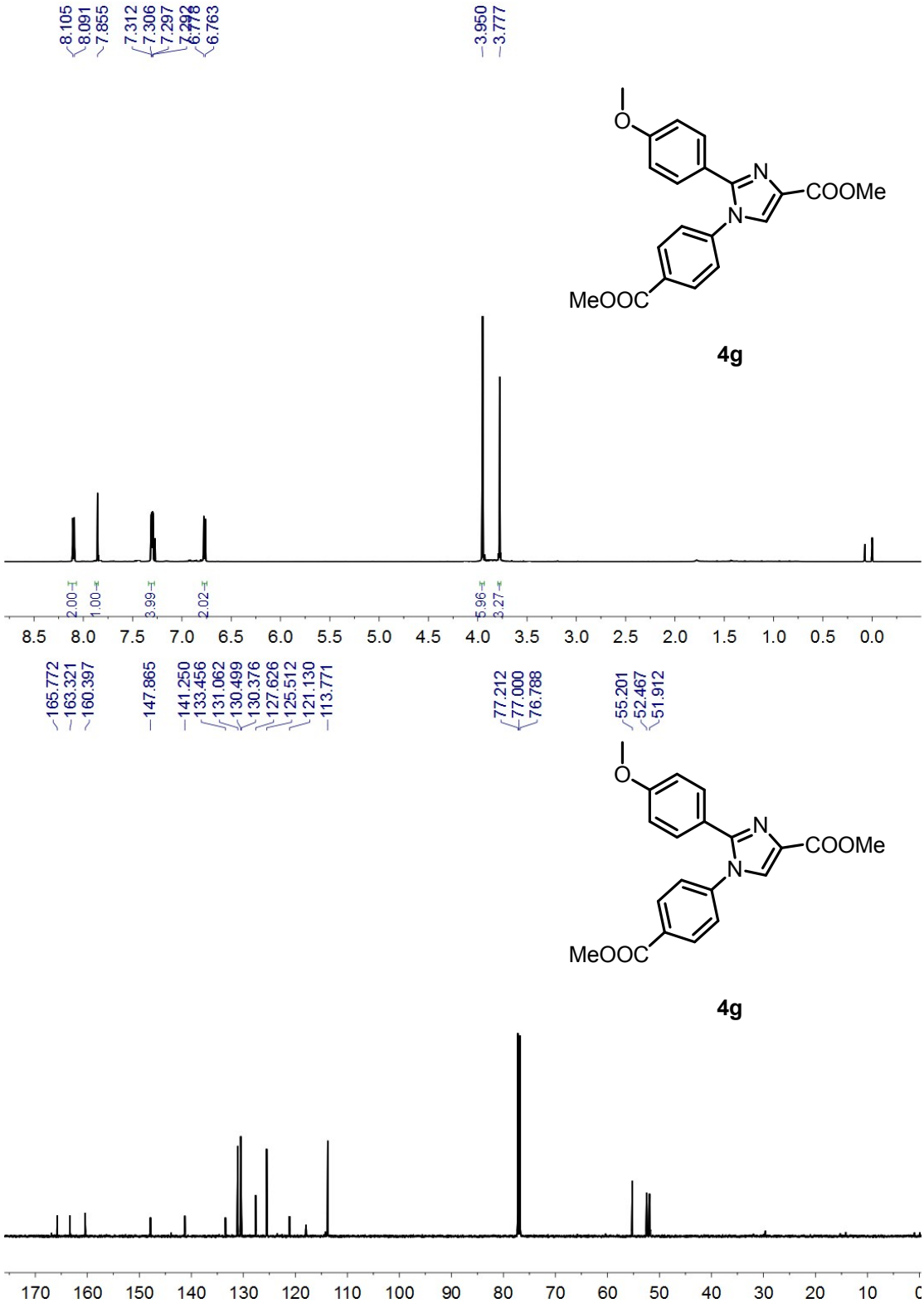


4f

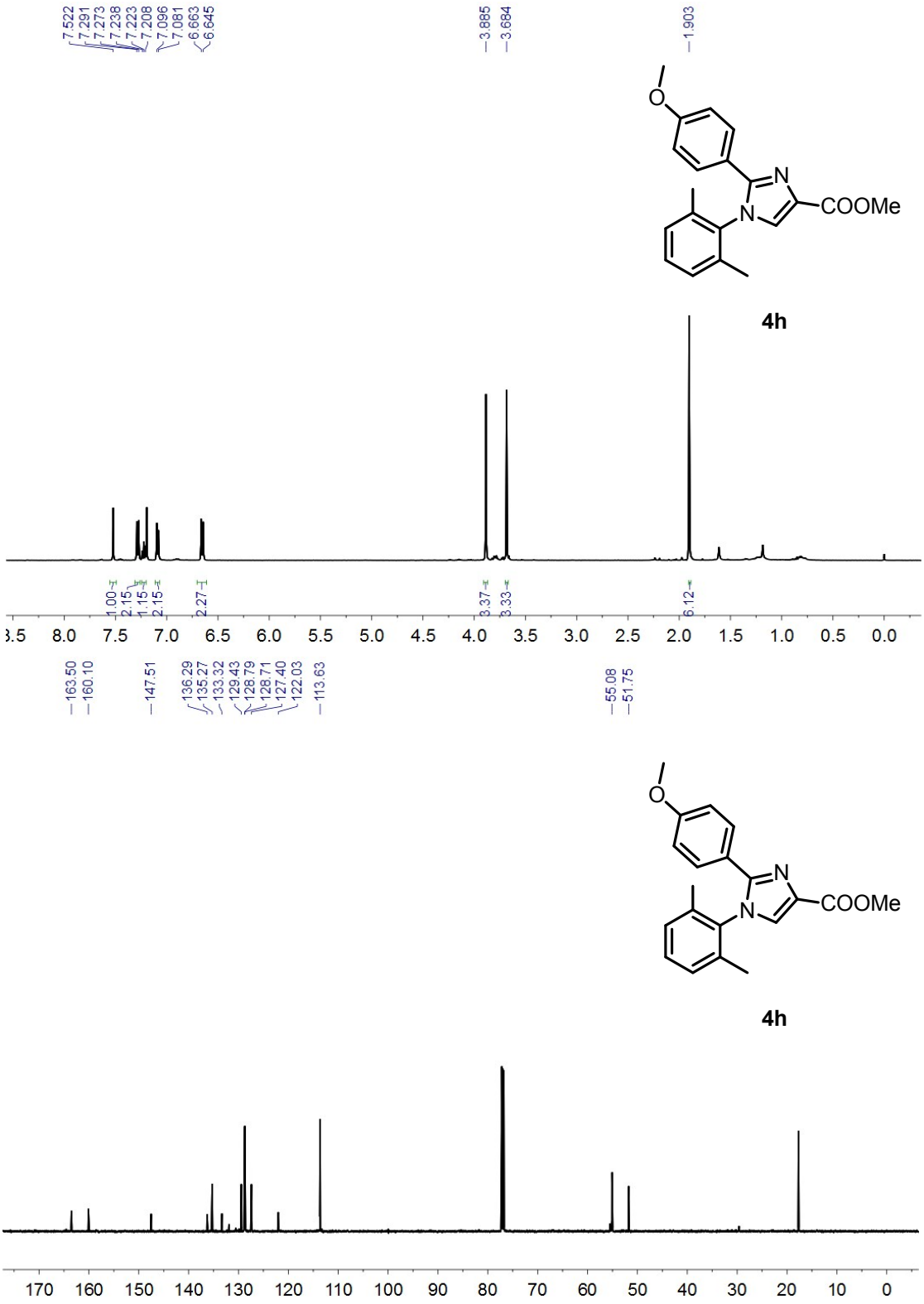


4f

4g **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

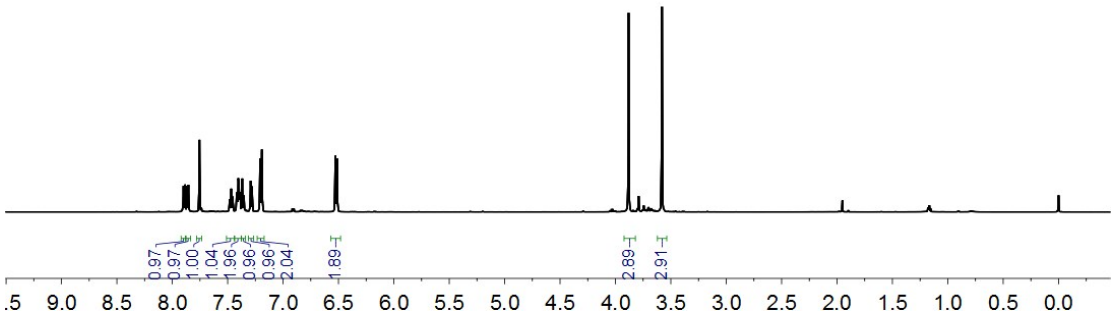


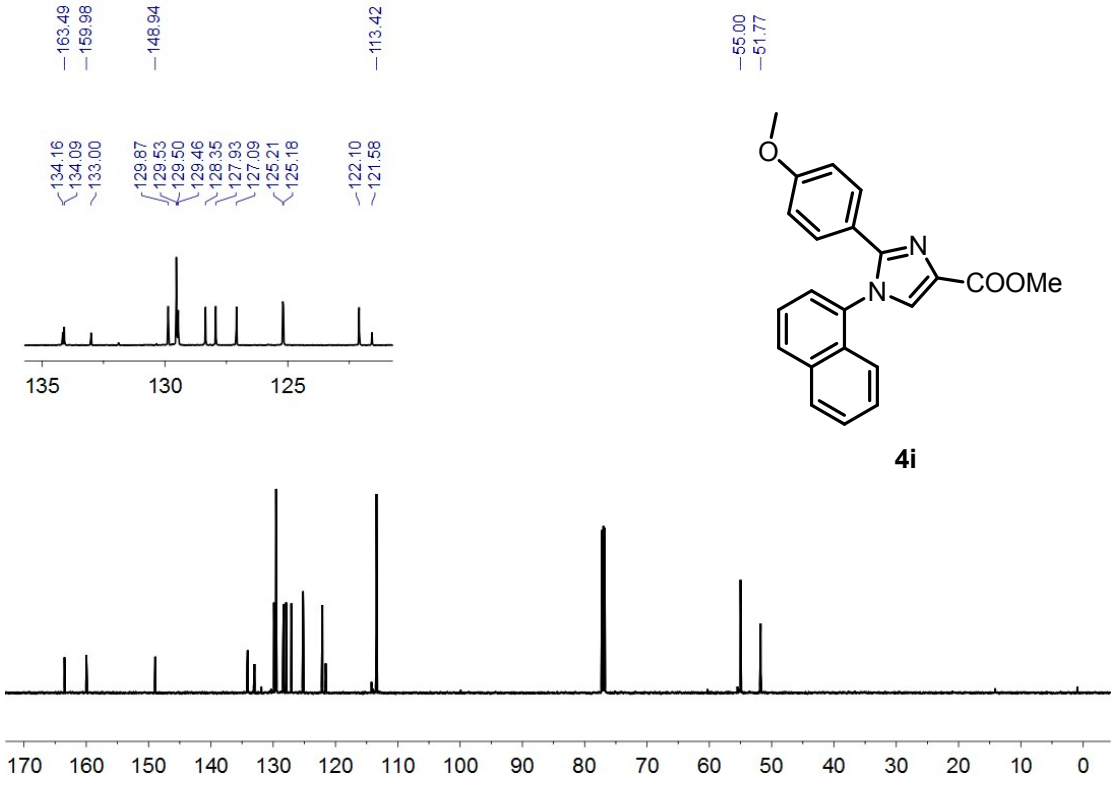
4h **^{1}H-NMR** (500 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



4i **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)

4i





4i

3aa **^{1}H-NMR** (600 MHz, DMSO) & **^{13}C-NMR** (DMSO, 150 MHz)