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Supporting information

Solvent controlled amidation of acid chlorides at room temperature: New route to access aromatic primary amides and imides amenable for late-stage functionalization

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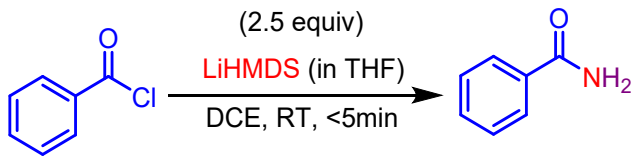
1. General Information

All the reaction were carried out in room temperature. All chemicals were purchased from Sigma-Aldrich, Avra, TCI, these were used without further purifications. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker BBFO (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to Tetramethylsilane (δ 0.00) or chloroform (δ = 7.19, singlet). Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Bruker BBFO (101 MHz) spectrometer. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). For Column chromatography 100-200 mesh silica gel used.

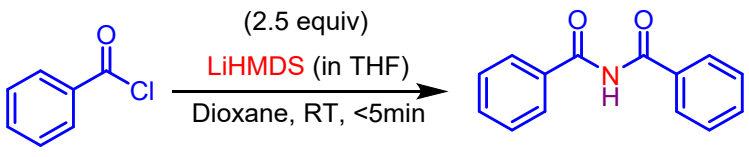
2.0 General procedure for the synthesis of primary amides



1 **2**

To a mixture of acid chlorides **1** (100 mg, 1 equiv) and lithium bis(trimethylsilyl)amide (LiHMDS in THF) (2.5 equiv) in a reaction tube with a magnetic stirring bar was added DCE (3 mL) and stirred at room temperature. The reaction mixture was stirred for 5 min at room temperature. After completion of reaction through TLC. Reaction mixture was workup with 1 M HCl solution, extracted with ethyl acetate and concentrated through in vacuo. The crude reaction mixture was purified by column chromatography using Ethyl Acetate-Hexane (50%) to give desired product **2**.

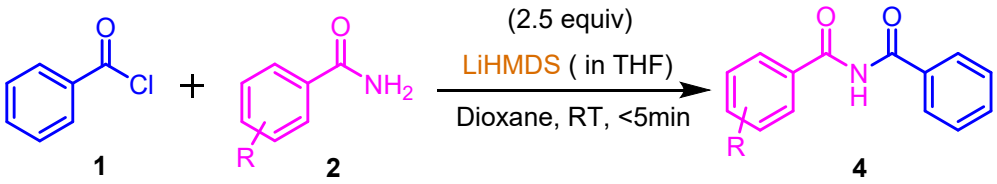
2.1 General procedure for the synthesis of symmetrical imides



1 **3**

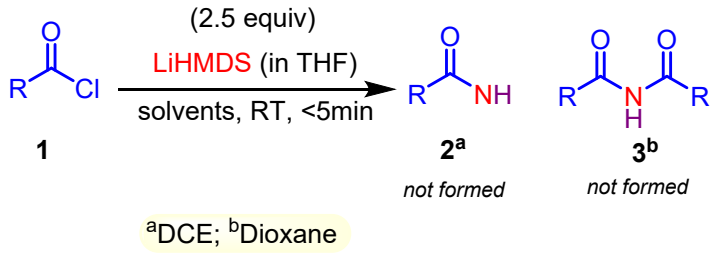
To a mixture of acid chlorides **1** (100 mg, 1 equiv) and lithium bis(trimethylsilyl)amide (LiHMDS in THF) (2.5 equiv) in a reaction tube with a magnetic stirring bar was added 1,4-dioxane and stirred at room temperature. The reaction mixture was stirred for 5 min at room temperature. After completion of reaction through TLC. Reaction mixture was workup with 1 M HCl solution, extracted with ethyl acetate and concentrated through in vacuo. The crude reaction mixture was purified by column chromatography using Ethyl Acetate-Hexane (25%) to give desired product **3**.

2.2 General procedure for the synthesis of unsymmetrical imides



To a mixture of acid chlorides **1** (100 mg, 1 equiv), aryl amides **2** (1.1 equiv) and lithium bis(trimethylsilyl)amide (LiHMDS in THF) (2.5 equiv) in a reaction tube with a magnetic stirring bar was added 1,4-dioxane and stirred at room temperature. The reaction mixture was stirred for 5 min at room temperature. After completion of reaction through TLC. Reaction mixture was workup with 1 M HCl solution, extracted with ethyl acetate and concentrated through in vacuo. The crude reaction mixture was purified by column chromatography using Ethyl Acetate-Hexane (24%) to give desired product **4a**.

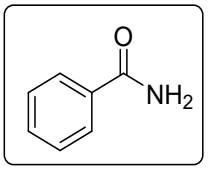
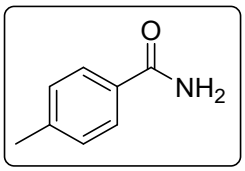
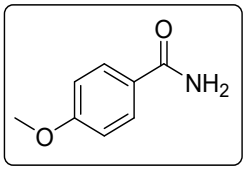
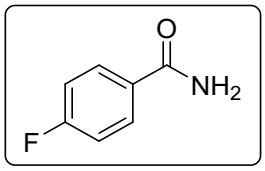
2.3 General procedure with aliphatic acid chlorides

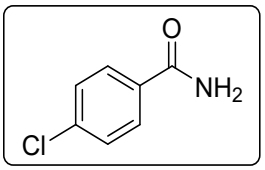
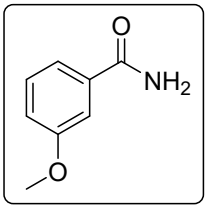
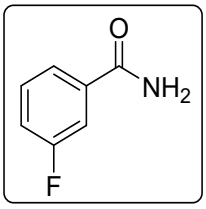
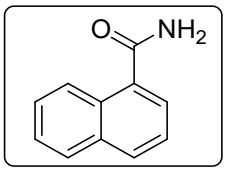


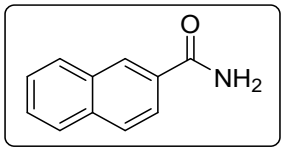
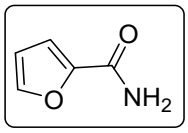
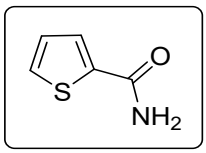
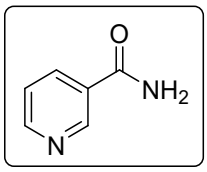
R= acetyl chlroride, Propionyl chloride, cyclohexanecarbonyl chloride, cyclopentanecarbonyl chloride, 2-cyclohexylacetyl chloride

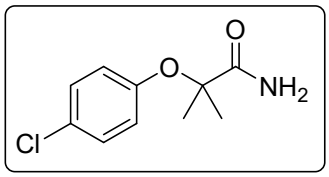
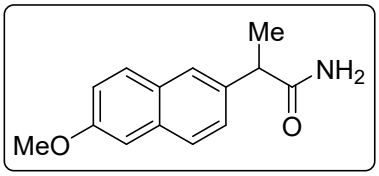
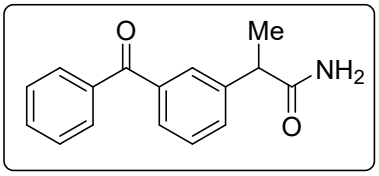
To a mixture of acid chlorides **1** (100 mg, 1 equiv) and lithium bis(trimethylsilyl)amide (LiHMDS in THF) (2.5 equiv) in a reaction tube with a magnetic stirring bar was added DCE (3 mL)/Dioxane (3mL) and stirred at room temperature. The reaction mixture was stirred for 5 min at room temperature. The reaction did not proceed.

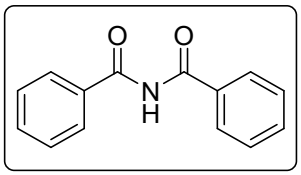
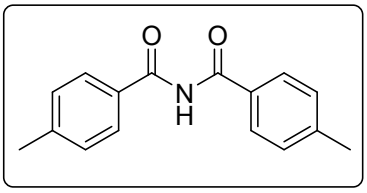
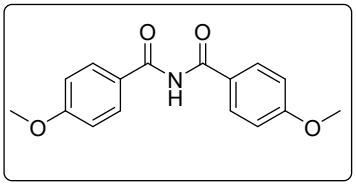
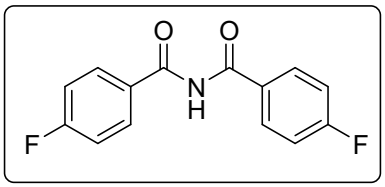
3. Characterization Data:

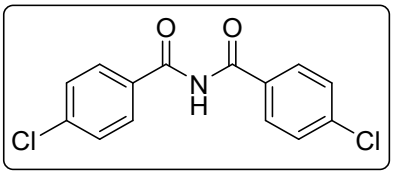
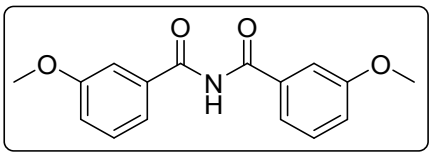
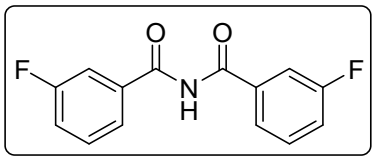
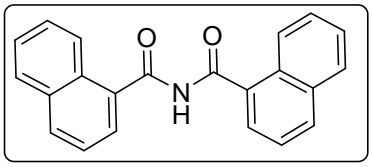
	**Benzamide 2a:**[1] white solid, (69 mg, 80%); Mp: 127–129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 6.25 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.8, 133.4, 132.0, 128.6, 127.4.
	**4-methylbenzamide 2b:**[1] white solid, (74 mg, 75%); Mp: 156–157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 5.89 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.5, 142.6, 130.5, 129.3, 127.4, 21.5.
	**4-methoxybenzamide 2c:**[1] white solid, (64 mg, 73%); Mp: 163–165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.81 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.8, 162.6, 129.3, 125.5, 113.8, 55.5.
	**4-fluorobenzamide 2d:**[1] white solid, 73 mg, 83%); Mp: 137–139 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.06 (t, *J* = 8.5 Hz, 2H), 5.94 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.2, 165.08 (d, *J* = 252.7 Hz), 129.8 (d, *J* = 9.1 Hz), 115.73 (d, *J* = 22.0 Hz)

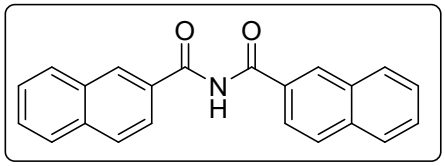
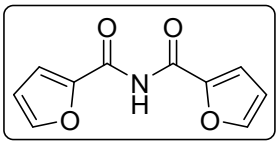
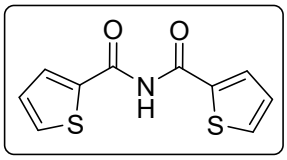
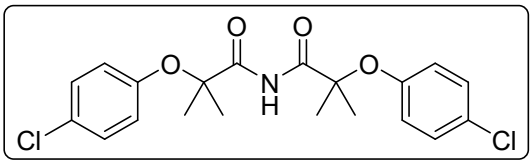
	^{19}F NMR (377 MHz, $CDCl_3$): δ -107.22 – -107.29 (m).
	**4-chlorobenzamide 2e:**[1] white solid, (77 mg, 86%); Mp: 179–180 °C; **^{1}H NMR** (400 MHz, DMSO): δ 8.05 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.45 (s, 1H). **^{13}C NMR** (101 MHz, DMSO): δ 167.3, 136.5, 133.5, 129.9, 128.8.
	**3-methoxybenzamide 2f:**[1] white solid, (63 mg, 72%); Mp: 120–121 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.30-7.26 (m, 2H), 7.01 – 6.99 (m, 1H), 6.08 (s, 1H), 5.93 (s, 1H), 3.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.4, 159.9, 134.7, 129.6, 119.2, 118.3, 112.6, 55.5.
	**3-fluorobenzamide 2g:**[1] white solid, (70 mg, 80%); Mp: 128–130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (t, *J* = 9.8 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 9.6 Hz, 1H), 6.10 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.2 (d, *J* = 2.4 Hz), 162.7 (d, *J* = 247.9 Hz), 135.5 (d, *J* = 6.9 Hz), 130.3 (d, *J* = 7.9 Hz), 122.8 (d, *J* = 3.1 Hz), 119.11 (d, *J* = 21.3 Hz), 114.76 (d, *J* = 23.0 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -111.63 – -111.65 (m).
	**1-naphthamide 2h:**[1]white solid, (68 mg, 76%); Mp: 198–200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.52 (dd, *J* = 8.5, 6.9, 1.6 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.42 (dd, *J* = 8.2, 7.1 Hz, 1H), 5.93

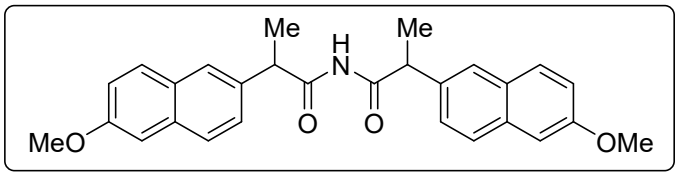
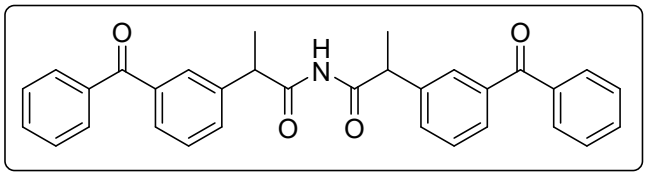
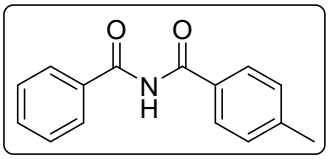
	(s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.5, 133.8, 133.1, 131.2, 130.1, 128.4, 127.3, 126.5, 125.4, 125.4, 124.6.
	**2-naphthamide 2i:**[1] White solid, (69 mg, 77%); Mp: 191–192 °C; **^{1}H NMR** (400 MHz, DMSO): δ 8.55 (s, 1H), 8.20 (s, 1H), 8.07 – 8.02 (m, 4H), 7.68 – 7.62 (m, 2H), 7.54 (s, 1H). **^{13}C NMR** (101 MHz, DMSO): δ 168.4, 134.6, 132.6, 132.1, 129.3, 128.3, 128.2, 128.1, 128.0, 127.1, 124.9.
	**Furan-2-carboxamide 2j:**[1] White solid, (62 mg, 73%); Mp: 142–144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.10 (s, 1H), 6.46 (s, 1H), 6.23 (s, 1H), 5.78 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.1, 147.4, 144.5, 115.3, 112.4.
	**Thiophene-2-carboxamide 2k:**[1] White solid, (61 mg, 71%); Mp: 182–183 °C; **^{1}H NMR** (400 MHz, DMSO): δ 7.97 (s, 1H), 7.75 – 7.73 (m, 2H), 7.38 (s, 1H), 7.14 – 7.12 (m, 1H). **^{13}C NMR** (101 MHz, DMSO): δ 163.4, 140.8, 131.4, 129.1, 128.4.
	**Nicotinamide 2l:**[1] white solid, (66 mg, 76%); Mp: 130–131 °C; **^{1}H NMR** (400 MHz, DMSO): δ 8.72 (s, 1H), 8.39 – 8.38 (m, 1H), 7.91 (s, 1H), 7.89 (s, 1H), 7.31 (s, 1H), 7.20 (t, *J* = 6.0 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO): δ 167.2, 152.4,

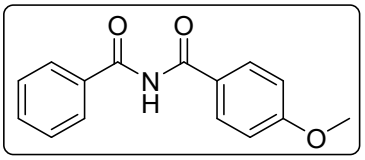
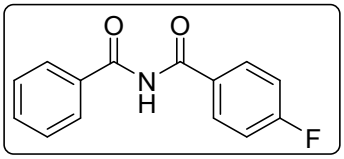
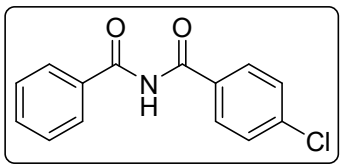
	149.0, 135.7, 130.1, 124.0.
	**2-(4-chlorophenoxy)-2-methylpropanamide 2p:** white solid, (50 mg, 55%); Mp: 128–129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.62 (s, 1H), 6.04 (s, 1H), 1.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 177.5, 152.8, 129.3, 129.0, 122.6, 81.7, 24.9. **HRMS** for **$C_{10}H_{12}ClNO_2$** [M+H] Calculated: **214.0634** Found: **214.0652**.
	**2-(6-methoxynaphthalen-2-yl)propenamide 2q:** white solid, (55 mg, 60%); Mp: 169–170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 3H), 7.39 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 5.43 (s, 1H), 5.36 (s, 1H), 3.92 (s, 3H), 3.74 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 176.8, 157.9, 136.3, 133.8, 129.2, 129.0, 127.7, 126.2, 126.1, 119.3, 105.7, 55.4, 46.6, 18.3. **HRMS** for **$C_{14}H_{15}NO_2$** [M-H] Calculated: **228.1024** Found: **228.1010**
	**2-(3-benzoylphenyl)propenamide 2r:** white solid, (41 mg, 45%); Mp: 139–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (s, 3H), 7.68-7.60 (m, 3H), 7.51-7.46 (m, 3H), 6.05 (s, 1H), 5.78 (s, 1H), 3.71 (d, *J* = 5.7 Hz, 1H), 1.56 (d, *J* = 6.1 Hz, 3H) **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.6, 176.4, 141.8, 138.0, 137.4, 132.7, 132.0, 130.1, 129.2, 129.1, 128.8, 128.4, 46.4, 18.5. **HRMS** for **$C_{16}H_{15}NO_2$** [M+H] Calculated: **254.1180** Found: **254.1168**

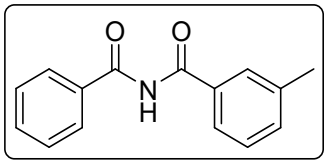
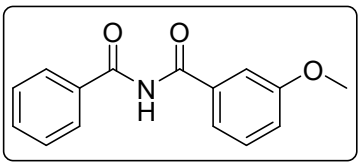
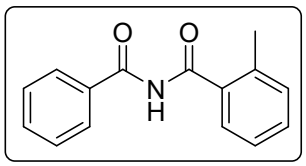
	***N*-benzoylbenzamide 3a:**[2] white solid, (50 mg, 63%); Mp: 150–152 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.81 (d, *J* = 7.1 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.3, 133.4, 133.2, 128.9, 127.9.
	**4-methyl-*N*-(4-methylbenzoyl)benzamide 3b:**[2] white solid, (48 mg, 59%); Mp: 149–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 2.37 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 169.5, 142.6, 130.5, 129.3, 127.4, 21.5.
	**4-methoxy-*N*-(4-methoxybenzoyl)benzamide 3c:**[2] white solid, (47 mg, 57%); Mp: 154–156 °C; **^{1}H NMR** (400 MHz, DMSO): δ 12.64 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 4H), 7.02 (d, *J* = 8.8 Hz, 4H), 3.82 (s, 6H). **^{13}C NMR** (101 MHz, DMSO): δ 167.5, 163.3, 131.8, 123.4, 114.3, 55.9.
	**4-fluoro-*N*-(4-fluorobenzoyl)benzamide 3d:**[2] white solid, (53 mg, 65%); Mp: 142–144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.82 (dd, *J* = 8.6, 5.2 Hz, 4H), 7.12 (t, *J* = 8.5 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.7, 130.8, 130.7, 129.3, 116.2, 116.0. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -104.51 – -104.58 (m).

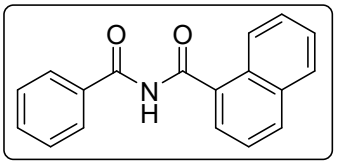
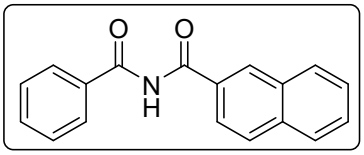
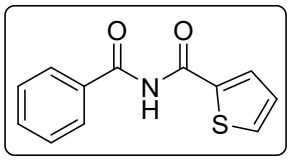
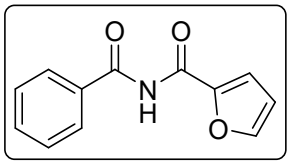
	**4-chloro-*N*-(4-chlorobenzoyl)benzamide 3e:**[2] White solid, (59 mg, 70%); Mp: 190–192 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 4H), 7.42 (d, *J* = 7.5 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.9, 139.8, 131.4, 129.6, 129.2.
	**3-methoxy-*N*-(3-methoxybenzoyl)benzamide 3f:**[2] white solid, (43 mg, 52%); Mp: 123–125 ^{o}C; **^{1}H NMR** (400 MHz, DMSO): δ 13.00 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 6H). **^{13}C NMR** (101 MHz, DMSO): δ 167.6, 159.7, 132.6, 130.2, 122.0, 119.4, 114.3, 55.7.
	**3-fluoro-*N*-(3-fluorobenzoyl)benzamide 3g:**[2] White solid, (49 mg, 60%); Mp: 135–136 ^{o}C; **^{1}H NMR** (400 MHz, DMSO): δ 11.45 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 4H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.50 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO): δ 166.8, 136.5, 131.1, 131.0, 125.3, 120.1, 119.9, 116.0, 115.8. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -110.62 (d, J = 6.9 Hz).
	***N*-(1-naphthoyl)-1-naphthamide 3h:**[2] white solid, (43 mg, 51%); Mp: 200–201 ^{o}C; **^{1}H NMR** (400 MHz, DMSO): δ 11.90 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 2H), 8.10 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 6.5 Hz, 2H), 7.64 – 7.58 (m, 6H). **^{13}C NMR** (101 MHz, DMSO): δ 169.4, 133.6,

	133.2, 131.6, 130.1, 128.9, 127.8, 127.2, 126.9, 125.3, 125.2.
	***N*-(2-naphthoyl)-2-naphthamide 3i:**[2] white solid, (47 mg, 55%); Mp: 193–195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.37 (s, 2H), 7.92 (dd, *J* = 8.2, 3.9 Hz, 4H), 7.88 – 7.84 (m, 4H), 7.59 – 7.51 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.6, 135.5, 132.5, 129.3, 129.1, 128.9, 128.7, 127.9, 127.2, 123.9.
	***N*-(furan-2-carbonyl)furan-2-carboxamide 3j:**[2] White solid, (32 mg, 41%); Mp: 145–146 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 7.52 (s, 2H), 7.33 (s, 2H), 6.56 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.5, 146.6, 145.3, 118.1, 113.3.
	***N*-(thiophene-2-carbonyl)thiophene-2-carboxamide 3k:**[2] White solid, (33 mg, 40%); Mp: 185–186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 7.72 (d, *J* = 3.7 Hz, 2H), 7.61 (d, *J* = 4.9 Hz, 2H), 7.10 (t, *J* = 4.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.5, 137.3, 133.5, 131.5, 128.1.
	**2-(4-chlorophenoxy)-N-(2-(4-chlorophenoxy)-2-methylpropanoyl)-2-methylpropanamide 3l:** White solid, (39 mg, 45%); Mp: 125–126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.37 (s, 1H), 7.17 (d, *J* = 8.9 Hz, 4H), 6.68 (d, *J* = 8.9 Hz, 4H), 1.50 (s, 12H). **13C NMR** (101 MHz, CDCl3): δ 172.7, 152.2, 129.5, 129.0, 121.7, 82.1, 24.5. **HRMS** for **$C_{20}H_{21}Cl_2NO_4$** [M+H] Calculated: **410.0925** Found: **410.0923**

	**2-(6-methoxynaphthalen-2-yl)-*N*-(2-(6-methoxynaphthalen-2-yl)propanoyl)propenamide 3m:** White solid, (40 mg, 46%); Mp: 159–160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 9.7 Hz, 6H), 7.39 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.19 (dd, *J* = 8.9, 2.5 Hz, 2H), 7.14 (d, *J* = 2.3 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 6H), 1.71 (d, *J* = 7.3 Hz, 6H). **13C NMR** (101 MHz, CDCl3): δ 174.0, 157.8, 134.8, 133.7, 129.2, 128.8, 127.5, 126.1, 126.1, 119.1, 105.5, 56.3, 47.1, 18.30. **HRMS** for **$C_{28}H_{27}NO_4$** [M+H] Calculated: **442.2018** Found: **442.2040**
	**2-(3-benzoylphenyl)-*N*-(2-(3-benzoylphenyl)propanoyl)propenamide 3n:** White solid, (32 mg, 36%); Mp: 132–134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 4H), 7.65 (d, *J* = 10.0 Hz, 4H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.38 – 7.31 (m, 4H), 4.27 (d, *J* = 6.8 Hz, 2H), 1.49 (d, *J* = 7.0 Hz, 6H). **13C NMR** (101 MHz, CDCl3): δ 196.1, 173.8, 140.1, 138.0, 137.3, 133.0, 131.5, 130.1, 129.4, 129.3, 128.8, 128.3, 47.0, 18.6. **HRMS** for **$C_{32}H_{27}NO_4$** [M+H] Calculated: **490.2018** Found: **490.2025**
	***N*-benzoyl-4-methylbenzamide 4a:**[2] Yellow solid, (147 mg, 87%); Mp: 106–107 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.79 (d, *J* = 7.1 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 6.7 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.6, 166.3, 144.0, 133.5, 133.0, 130.5, 129.6, 128.9, 128.1, 128.0, 21.7.

	***N*-benzoyl-4-methoxybenzamide 4b:**[2] White solid, (132 mg, 88%); Mp: 168–169 °C; **^{1}H NMR** (400 MHz, DMSO) δ 11.17 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.52 (t, *J* = 7.1 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, DMSO): δ 168.4, 167.2, 163.3, 134.5, 132.9, 131.4, 129.0, 128.8, 126.2, 114.1, 56.0.
	***N*-benzoyl-4-fluorobenzamide 4c:**[2] White solid, (144 mg, 94%); Mp: 128–129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.83 – 7.78 (m, 4H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 8.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.9, 166.5, 166.0, 164.4, 133.2, 133.2, 130.9, 130.8, 129.5, 129.5, 128.9, 128.0, 116.1, 115.9. **^{19}F NMR** (377 MHz, $CDCl_3$): δ -104.85 (d, J = 6.5 Hz).
	***N*-benzoyl-4-chlorobenzamide 4d:**[2] White solid, (141 mg, 95%); Mp: 126–127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 9.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.5, 166.2, 139.5, 133.3, 133.1, 131.7, 129.6, 129.1, 128.9, 128.0.

	***N*-benzoyl-3-methylbenzamide 4e:**[2] White Solid, (125 mg, 81%); Mp: 95–97 °C; **^{1}H NMR** (400 MHz, DMSO): δ 11.28 (s, 1H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.75 (s, 1H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.64 (t, *J* = 6.8 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.47 – 7.39 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, DMSO): δ 168.2, 168.1, 138.2, 134.4, 134.2, 133.7, 133.0, 129.5, 129.1, 128.8, 128.8, 126.3, 21.3.
	***N*-benzoyl-3-methoxybenzamide 4f:**[2] White Solid, (123 mg, 82%); Mp: 166–167 °C; **^{1}H NMR** (400 MHz, DMSO): δ 11.30 (s, 1H), 7.90 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.46 – 7.42 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, DMSO): δ 168.3, 167.7, 159.6, 135.6, 134.4, 133.1, 130.1, 129.1, 128.8, 121.3, 119.1, 114.0, 55.9.
	***N*-benzoyl-2-methylbenzamide 4g:**[2] White solid, (124 mg, 80%); Mp: 152–153 °C; **^{1}H NMR** (400 MHz, DMSO): δ 11.45 (s, 1H), 7.92 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 6.9 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.31– 7.27 (m, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, DMSO): δ 170.7, 167.2, 136.4, 135.9, 133.7, 133.3, 131.0, 130.6, 129.1, 128.9, 128.0, 126.0, 19.8.
	***N*-benzoyl-1-naphthamide 4h:**[2] White Solid,

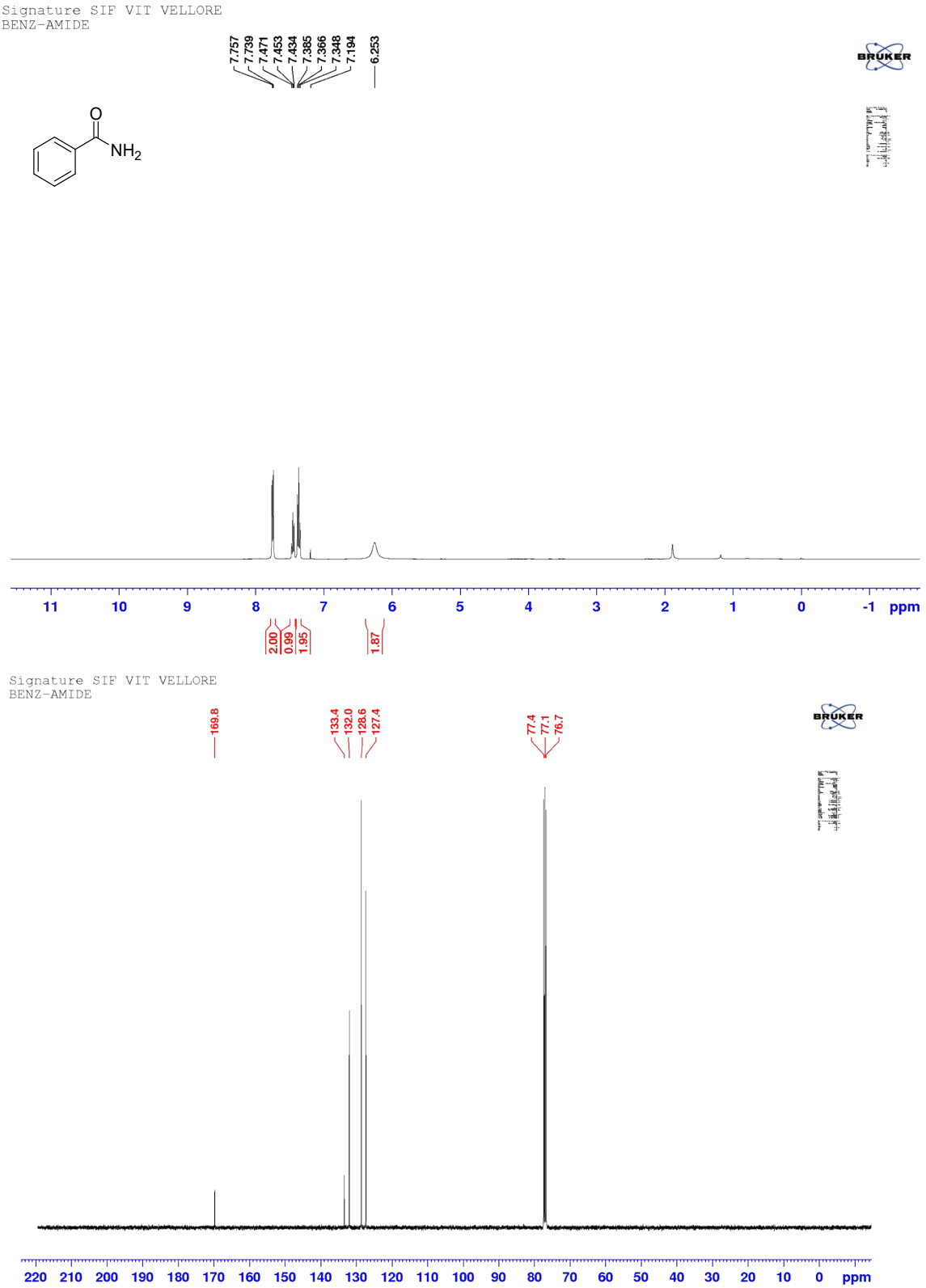
	(122 mg, 85%); Mp: 128–129 °C; **^{1}H NMR** (400 MHz, DMSO): δ 11.68 (s, 1H), 8.17 (d, *J* = 6.8 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 6.5 Hz, 1H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.64 – 7.58 (m, 4H), 7.52 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO): δ 170.2, 167.3, 133.9, 133.7, 133.6, 133.3, 131.3, 130.0, 129.1, 128.9, 127.7, 126.8, 126.7, 125.4, 125.1.
	***N*-benzoyl-2-naphthamide 4i:**[2] White solid, (119 mg, 83%); Mp: 147–148 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 8.31 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 4H)., 7.56 – 7.49 (m, 3H), 7.44 (t, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.6, 166.6, 135.5, 133.4, 133.1, 132.4, 130.5, 129.3, 129.1, 128.9, 128.9, 128.6, 128.1, 127.9, 127.2, 123.9.
	***N*-benzoylthiophene-2-carboxamide 4j:**[2] White solid, (130 mg, 82%); Mp: 118–119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.73 (s, 1H), 7.59 (s, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.09 (d, *J* = 3.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.4, 159.9, 137.5, 133.5, 133.4, 133.1, 131.3, 128.8, 128.2, 128.0.
	***N*-benzoylfuran-2-carboxamide 4k:**[2] White Solid, (137 mg, 83%); Mp: 102–104 °C **^{1}H NMR** (400 MHz, DMSO): δ 11.12 (s, 1H), 8.01 (s, 1H), 7.87 (d, *J* = 6.9 Hz, 2H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.60 (s, 1H), 7.54 (t, *J* = 6.6 Hz, 2H), 6.74 (s, 1H). **^{13}C NMR** (101 MHz, DMSO): δ 167.7, 157.2, 148.0, 146.8, 134.3, 133.1, 129.0, 128.9, 118.2, 112.8.

4. References:

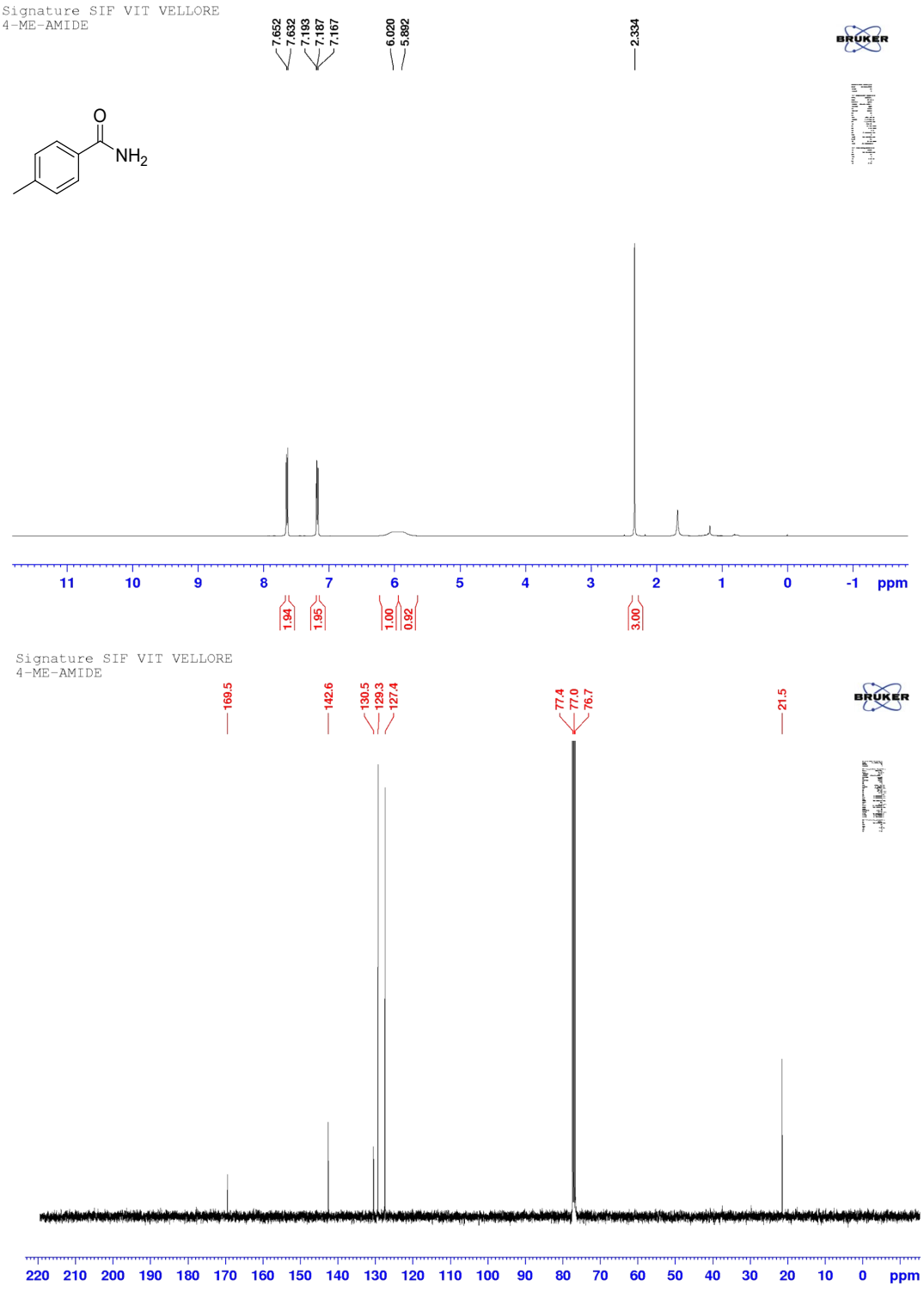
(1) Y. Guo, R. Wang, J. Kang, Y. Ma, C. Xu, J. Li and X. Chen, Efficient synthesis of primary and secondary amides *via* reacting esters with alkali metal amidoboranes, *Nat. Commun*. 2021, **12**, 1-9.

(2) J. Li, J. Yao, L. Chen, D. Zou, P. J. Walsh and G. Liang, Chemoselective acylation of *N*-acylglutarimides with *N*-acylpyrroles and aryl esters under transition-metal-free conditions. *Org. Chem. Front.* 2021, **8**, 6344-6349.

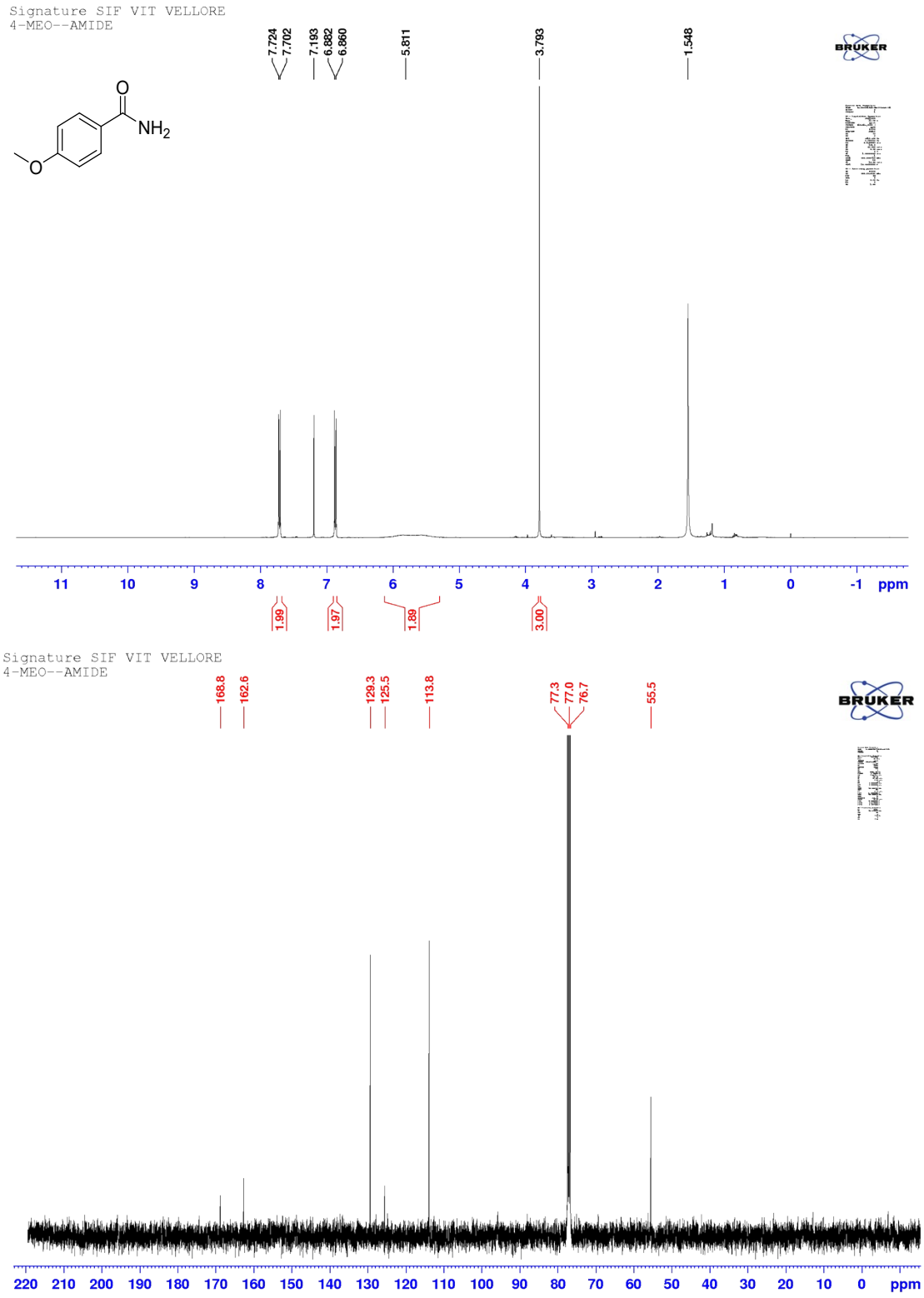
5. ^{1}H & ^{13}C NMR Spectra



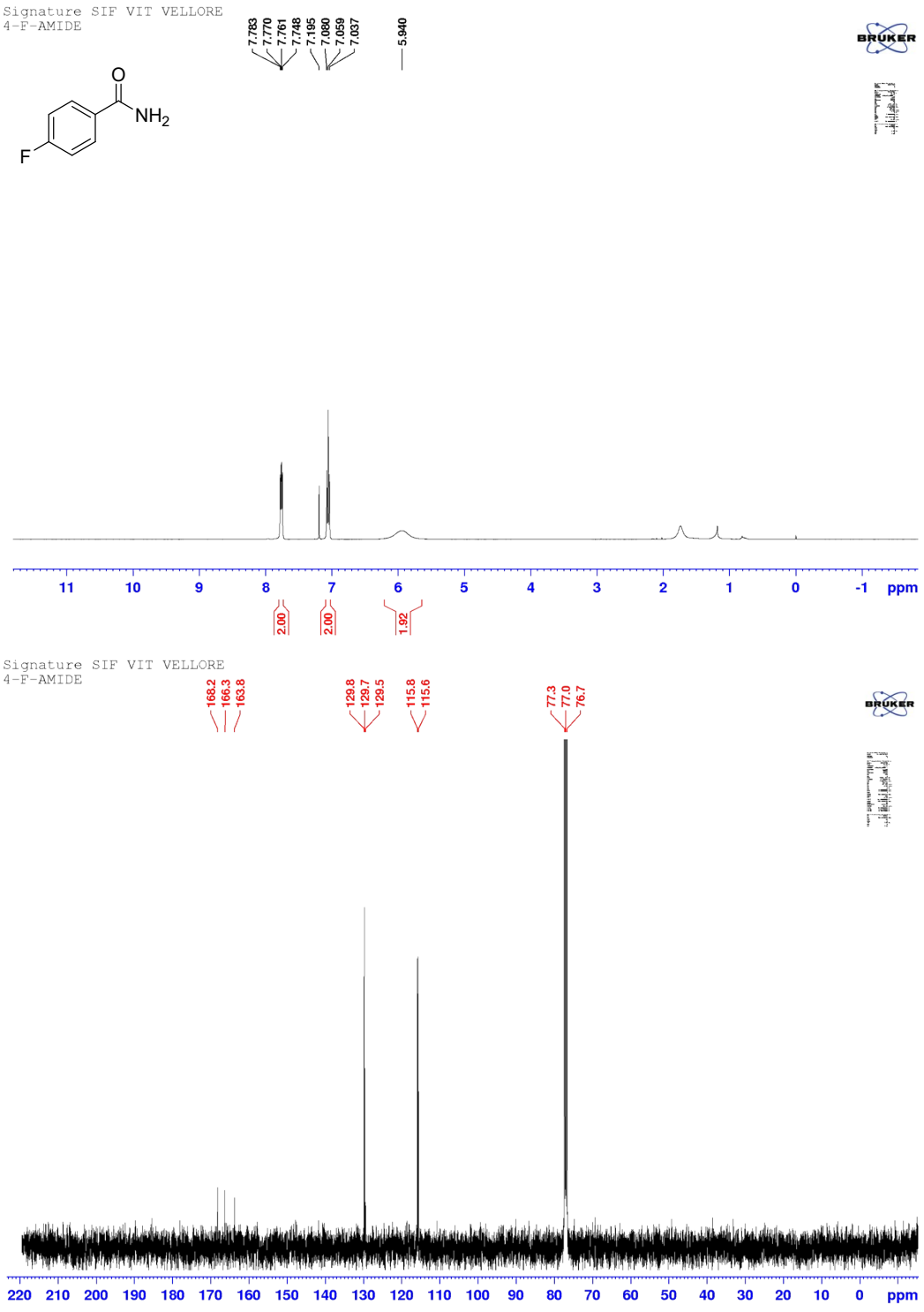
Supplementary Figure 1. ^{1}H NMR and ^{13}C NMR spectrum of benzamide **2a**



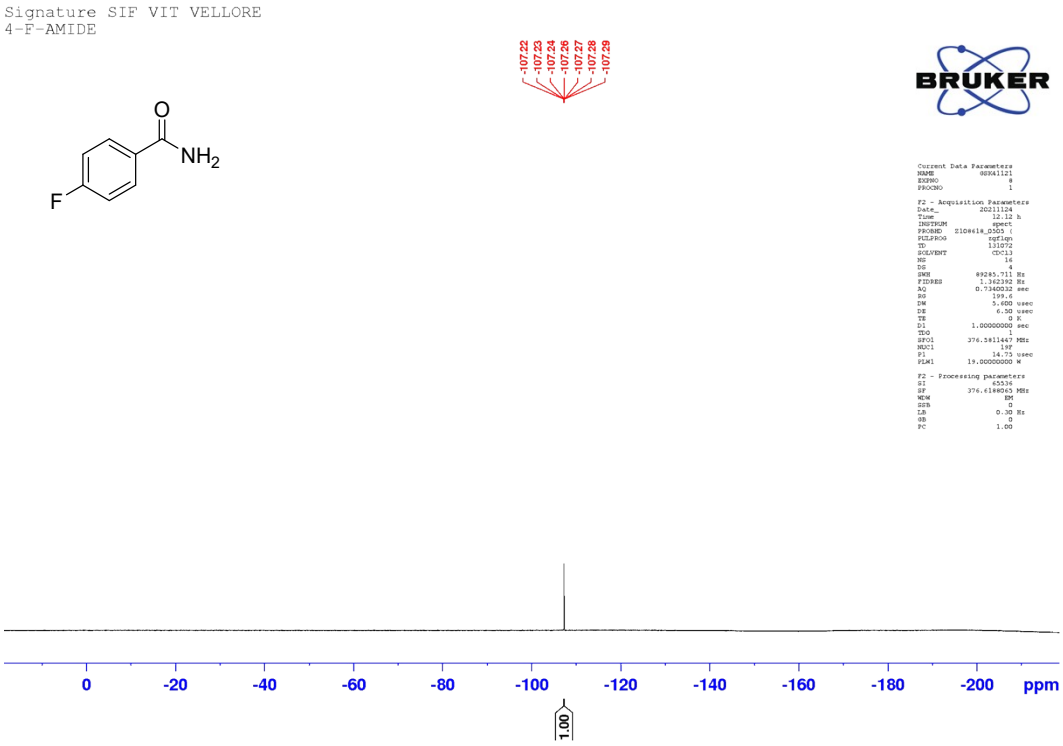
Supplementary Figure 2. ^{1}H NMR and ^{13}C NMR spectrum of 4-methylbenzamide **2b**



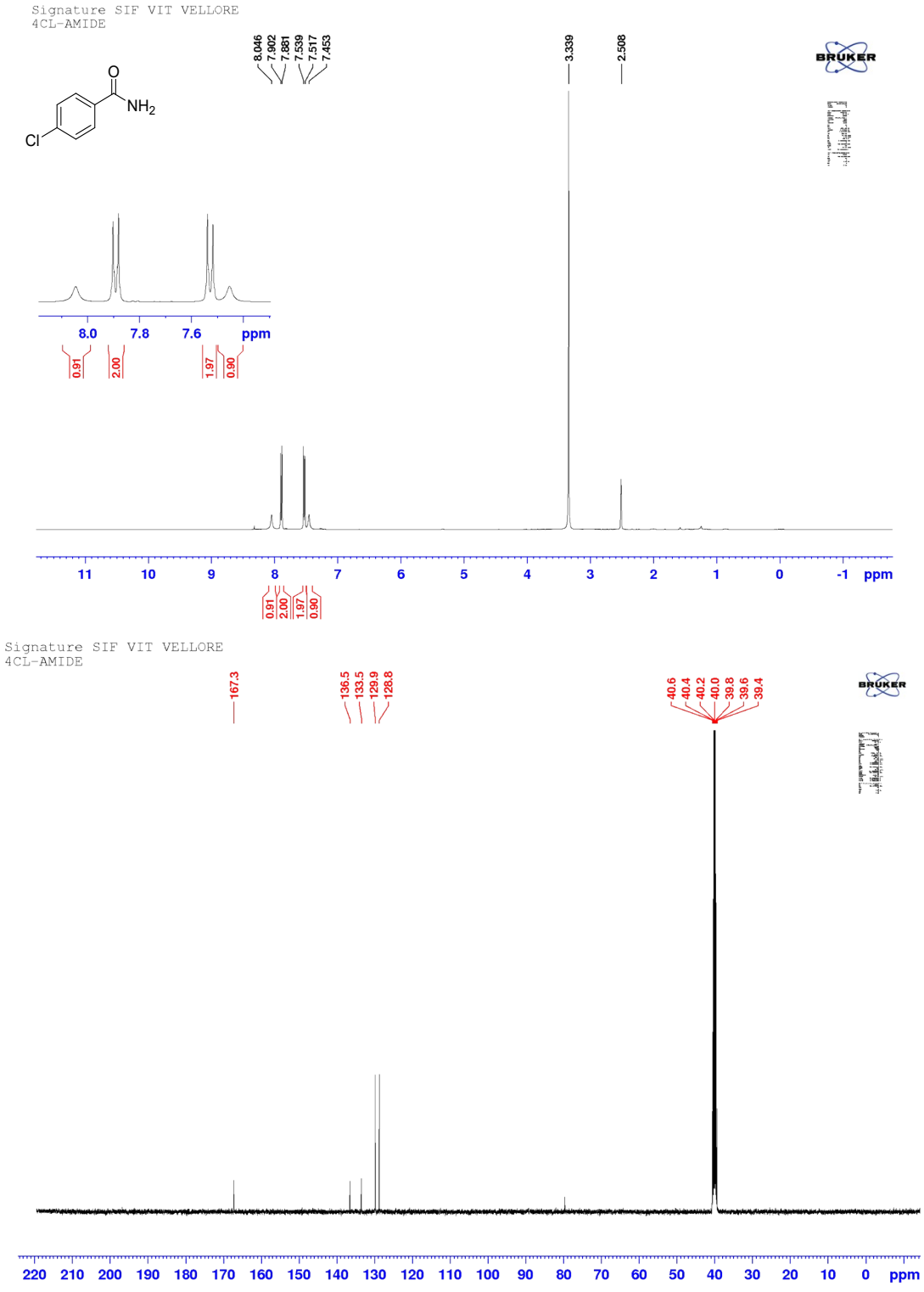
Supplementary Figure 3. ^{1}H NMR and ^{13}C NMR spectrum of 4-methoxybenzamide **2c**



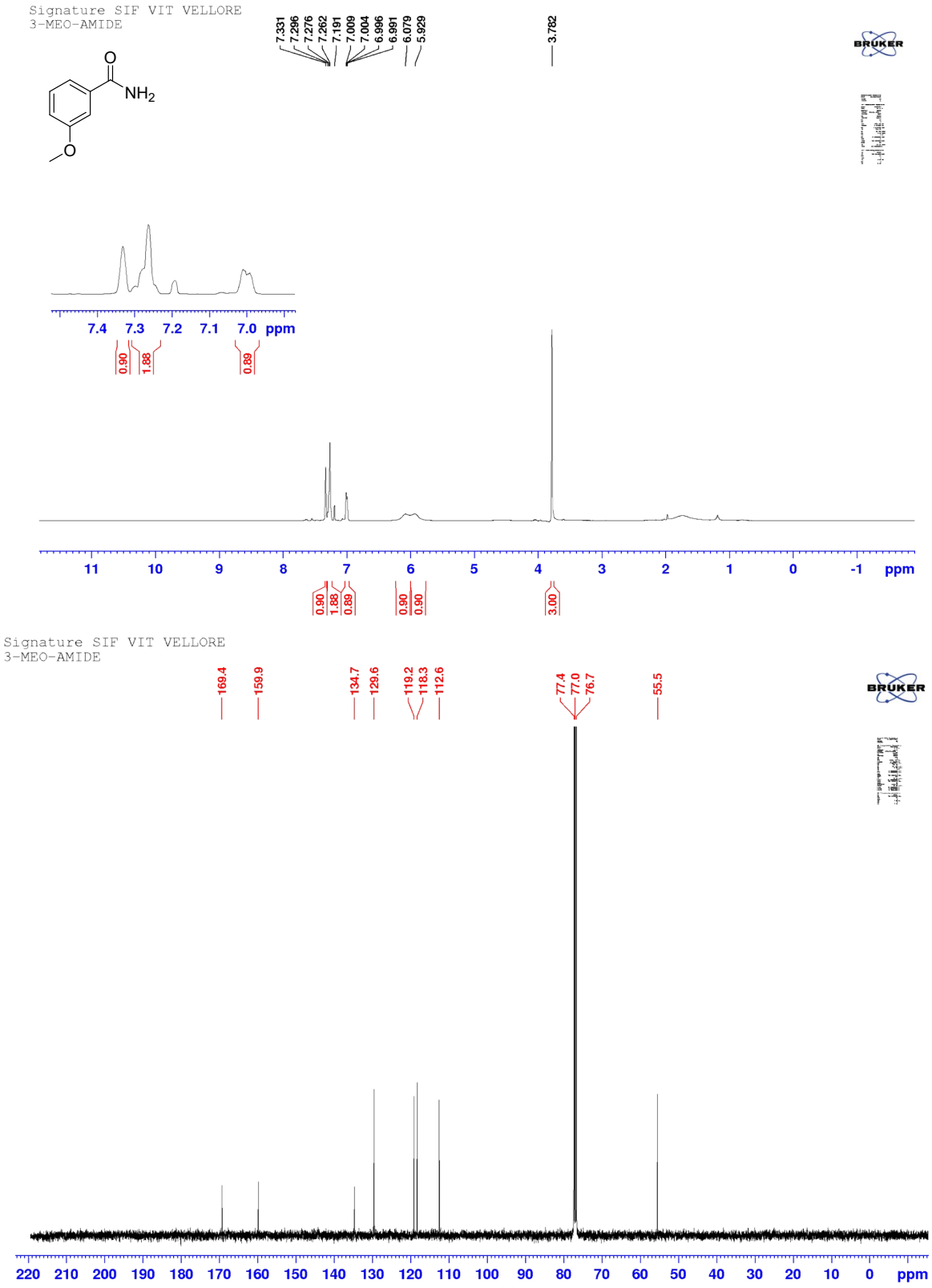
Supplementary Figure 4. ^{1}H NMR and ^{13}C NMR spectrum of 4-fluorobenzamide **2d**



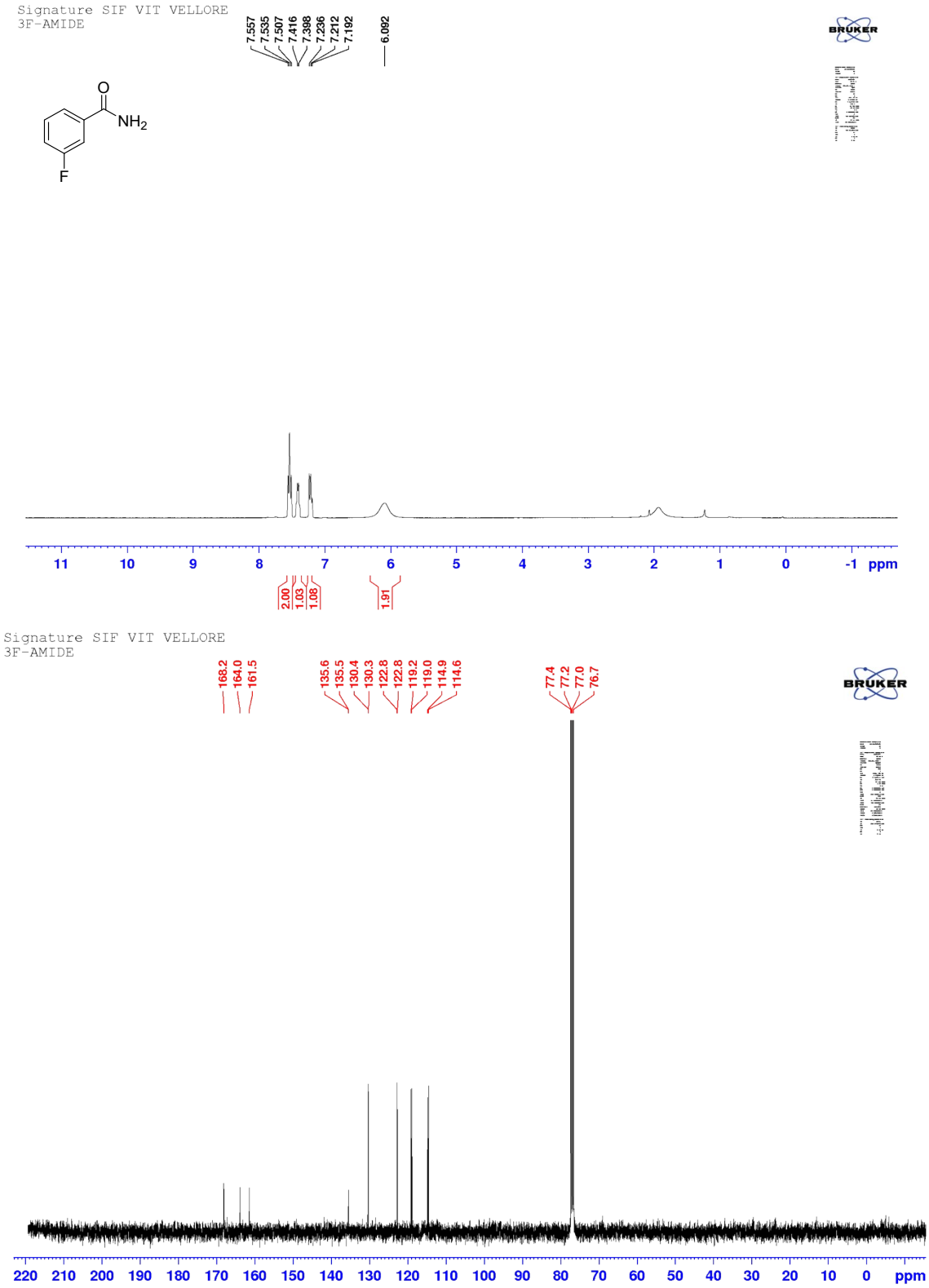
Supplementary Figure 5. ^{19}F NMR spectrum of 4-fluorobenzamide **2d**



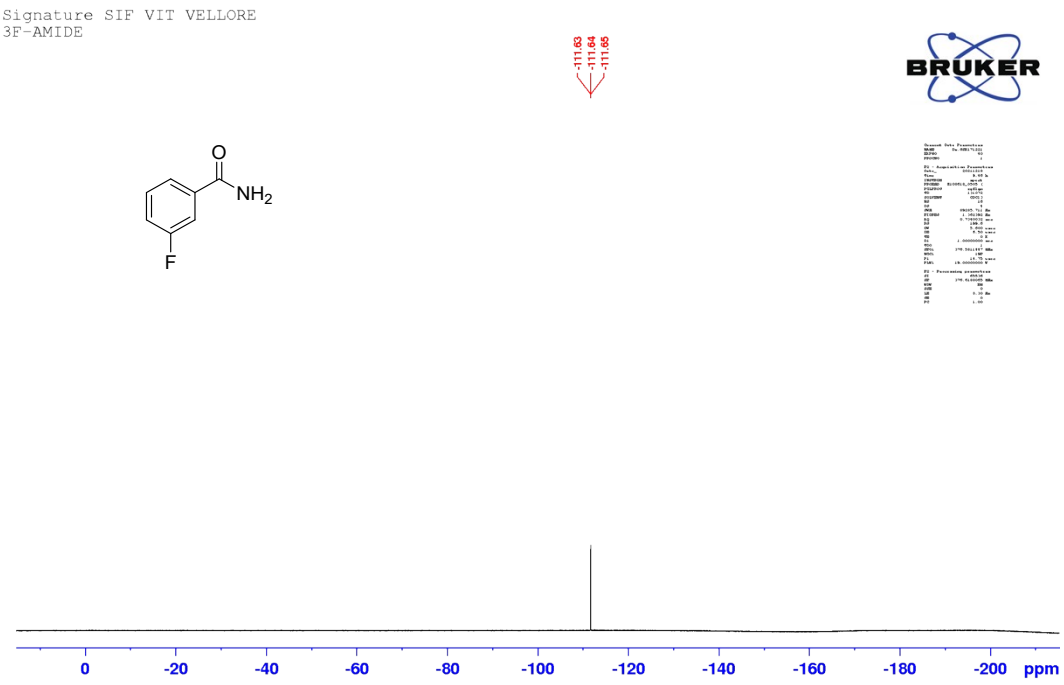
Supplementary Figure 6. ^{1}H NMR and ^{13}C NMR spectrum of 4-chlorobenzamide **2e**



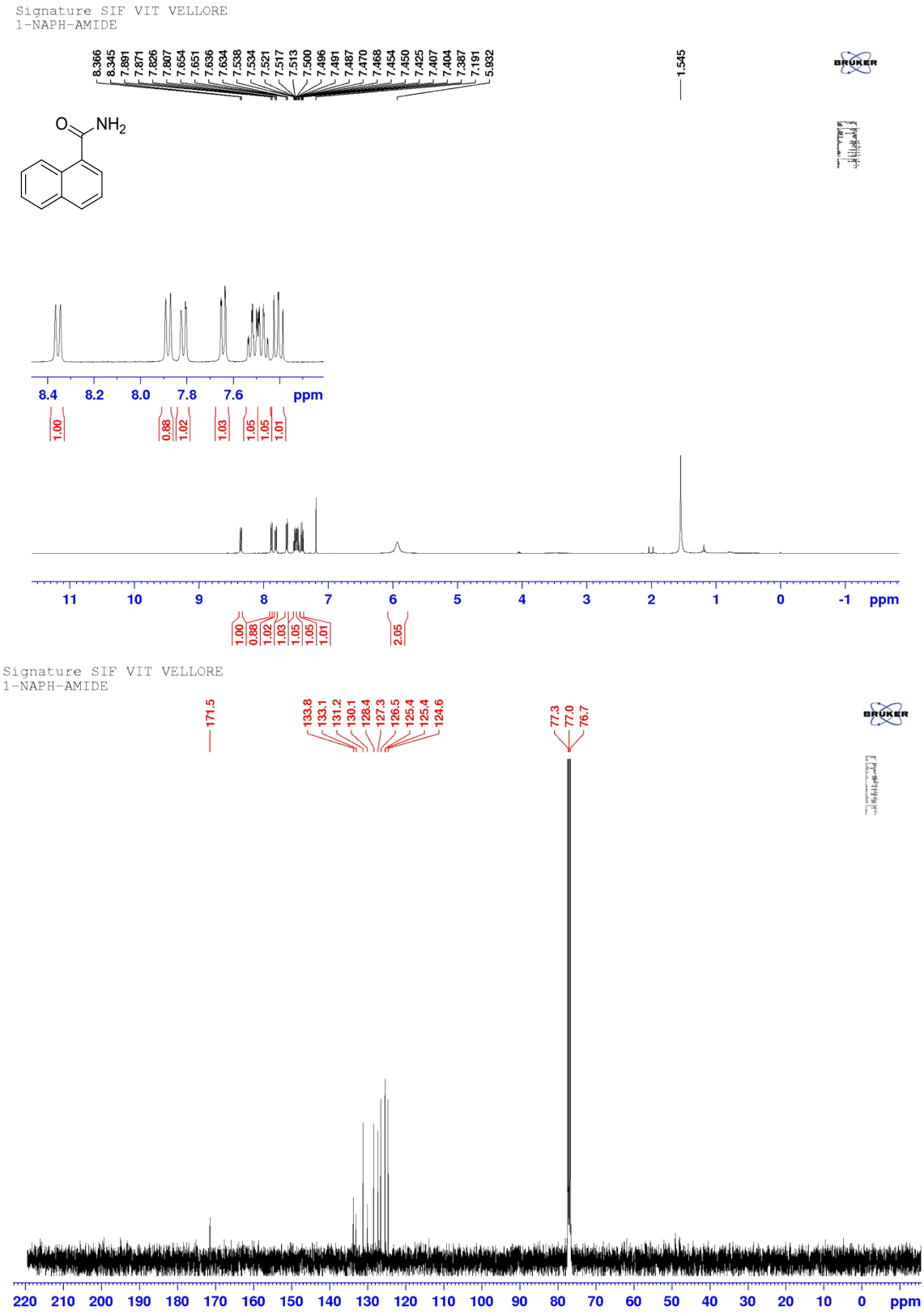
Supplementary Figure 7. ^{1}H NMR and ^{13}C NMR spectrum of 3-methoxybenzamide **2f**



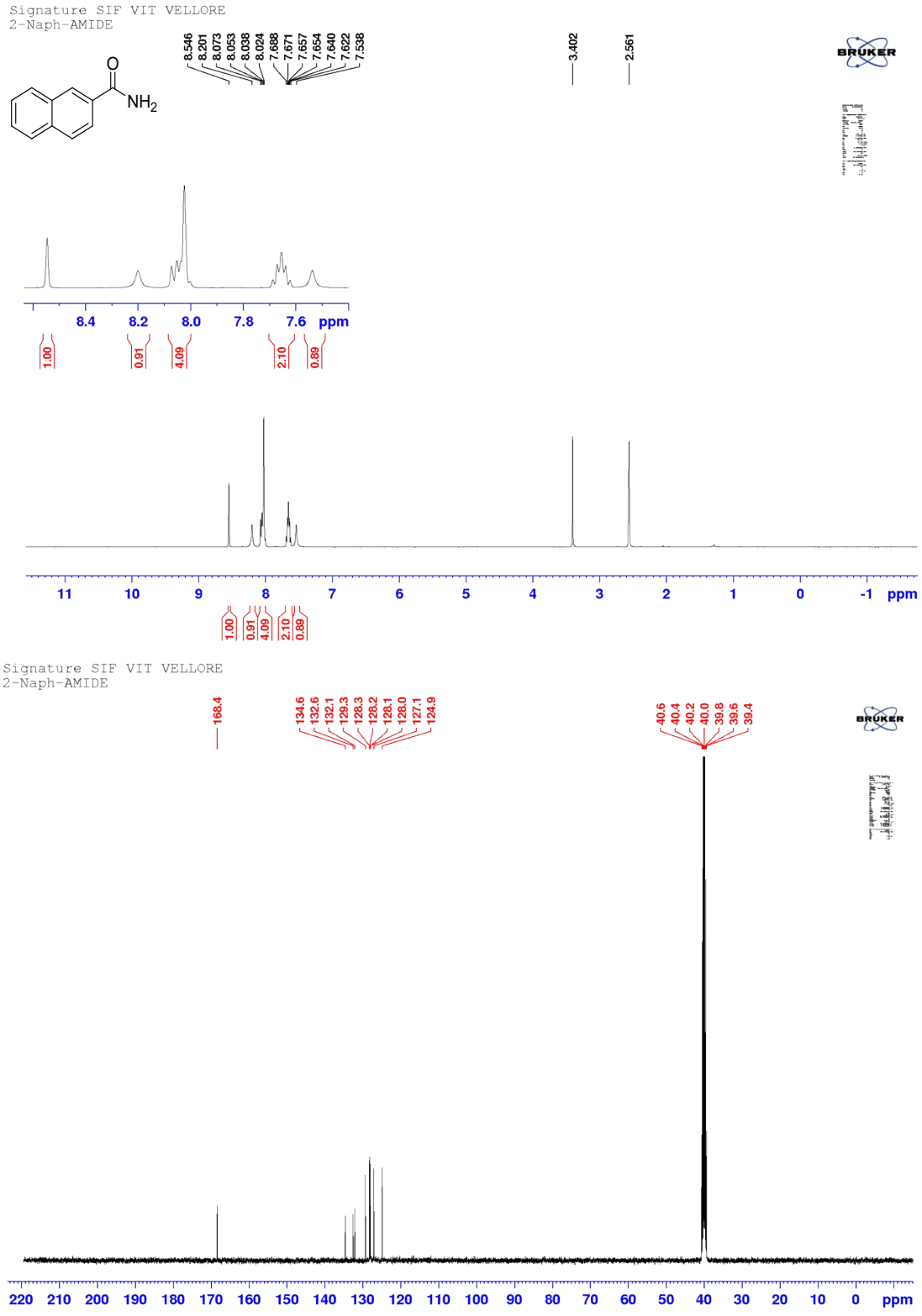
Supplementary Figure 8. ^{1}H NMR and ^{13}C NMR spectrum of 3-fluorobenzamide **2g**



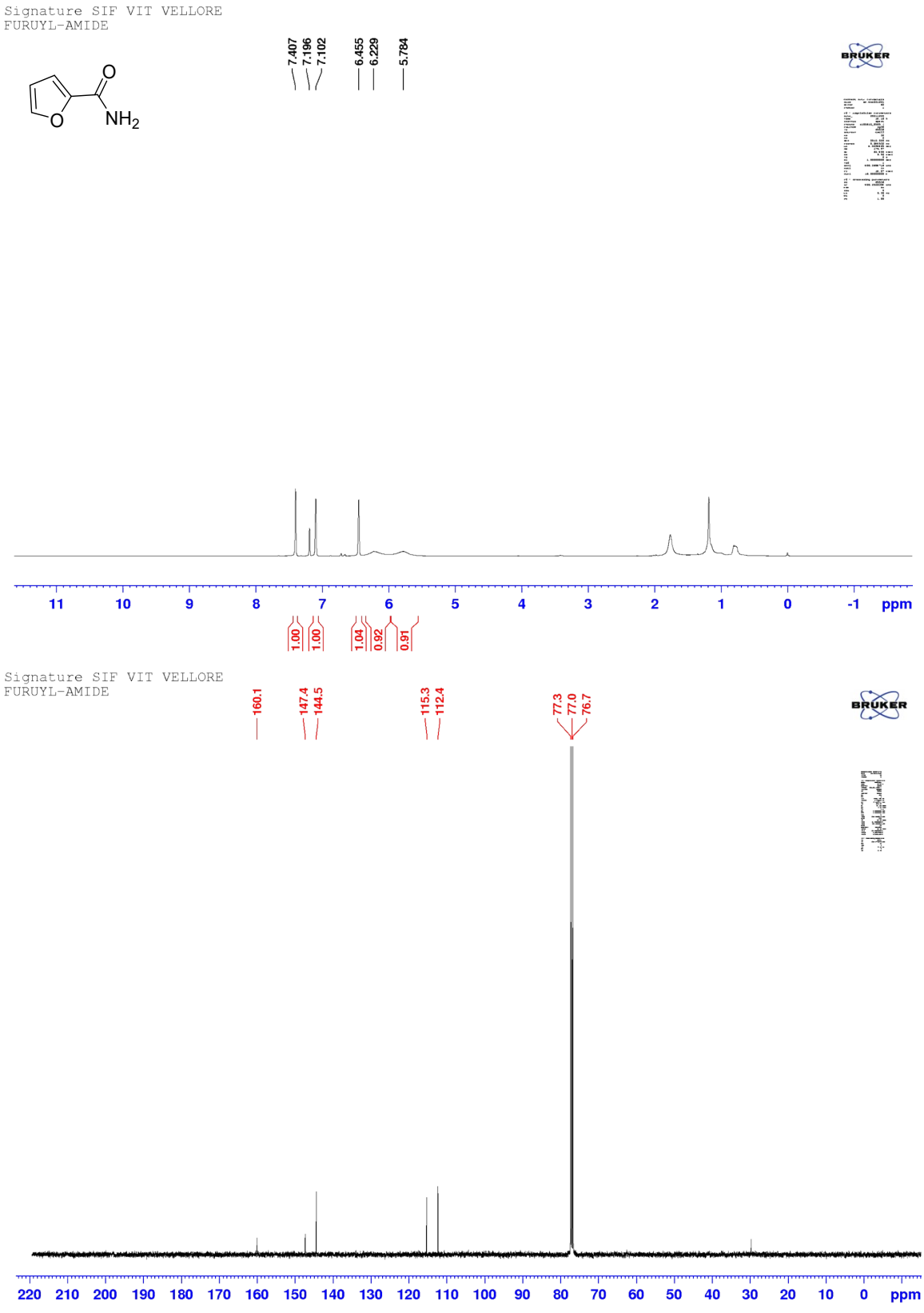
Supplementary Figure 9. ^{19}F NMR spectrum of 3-fluorobenzamide **2g**



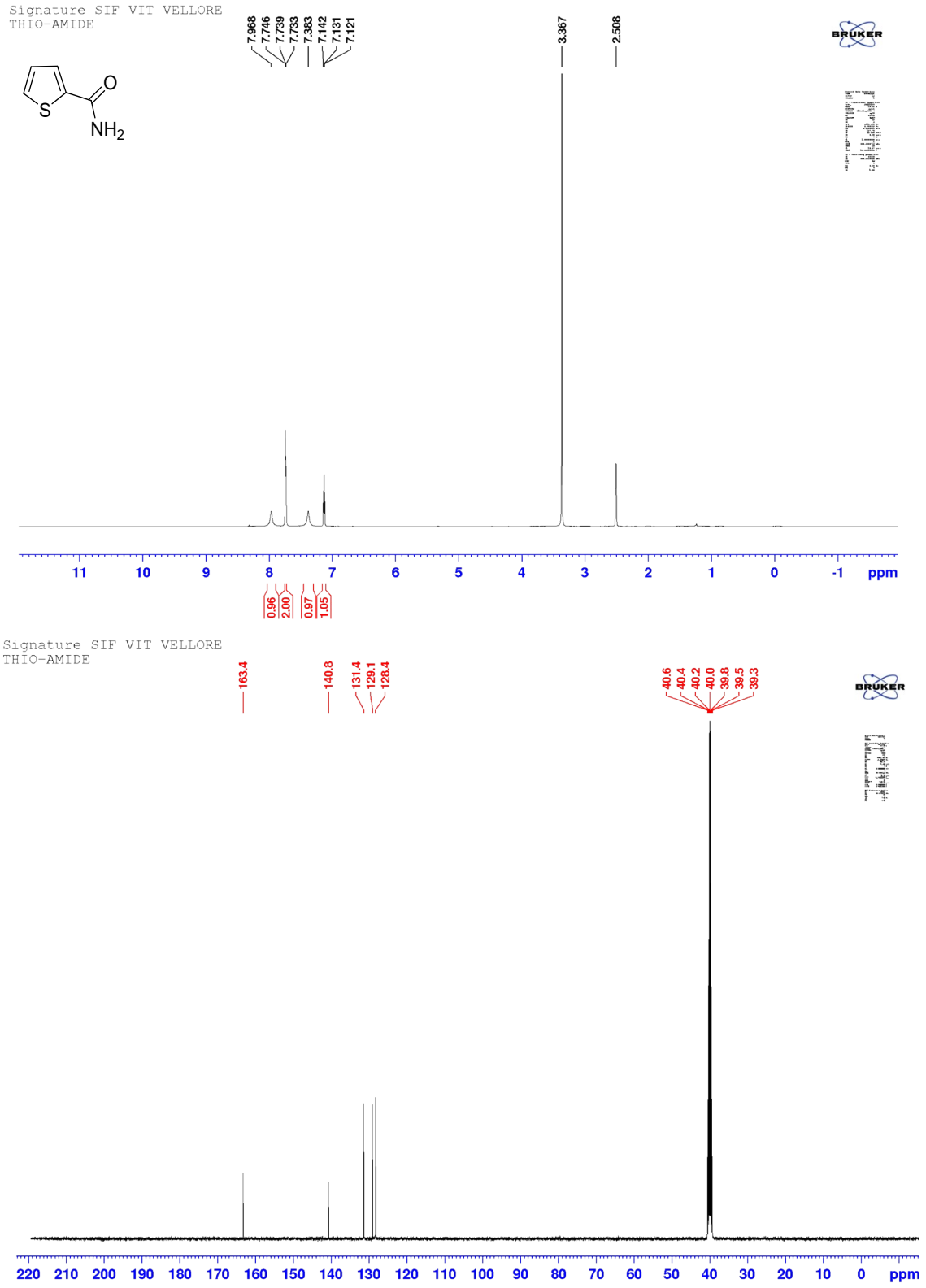
Supplementary Figure 10. ^{1}H NMR and ^{13}C NMR spectrum of 1-naphthamide **2h**



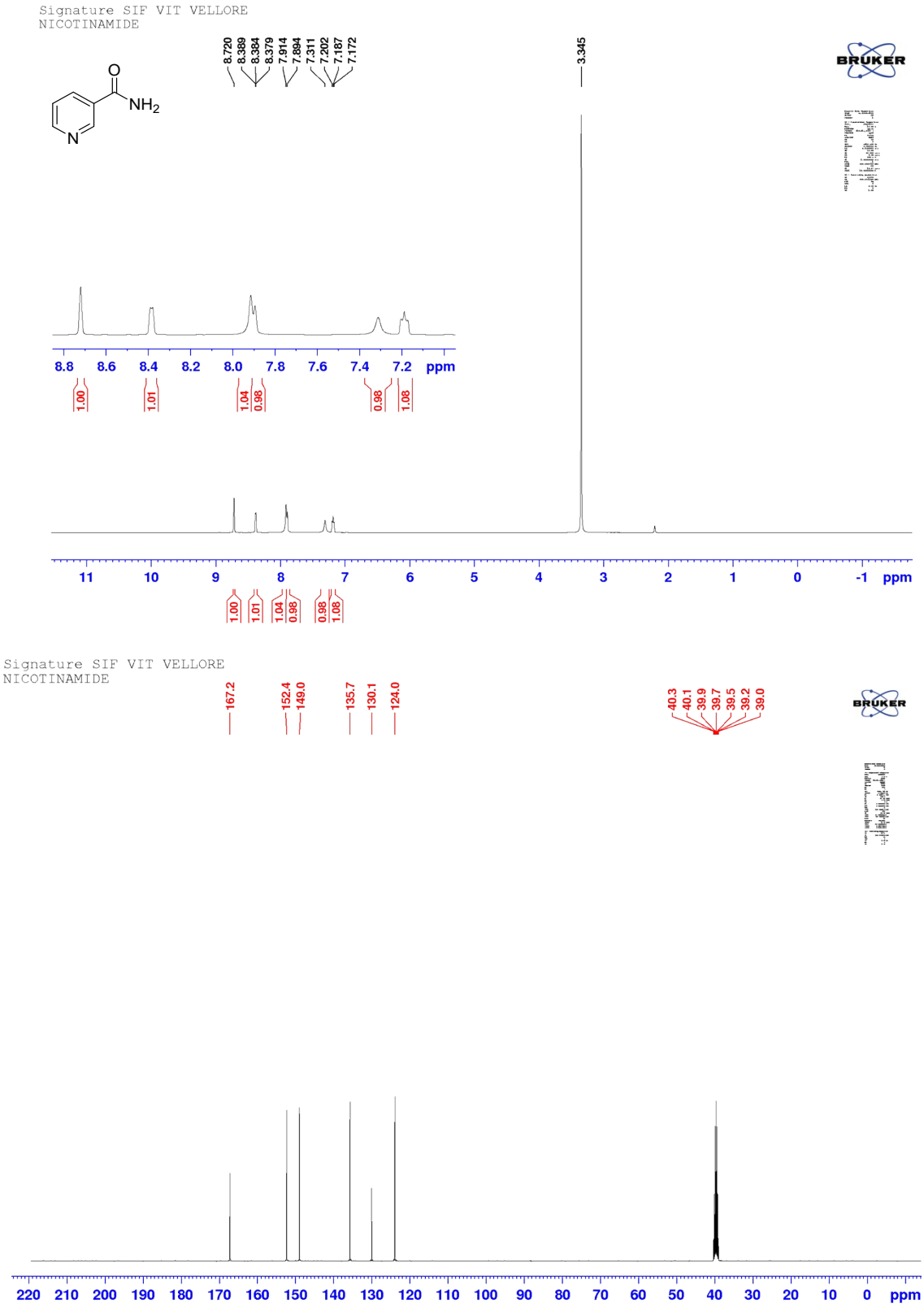
Supplementary Figure 11. ^{1}H NMR and ^{13}C NMR spectrum of 2-naphthamide **2i**



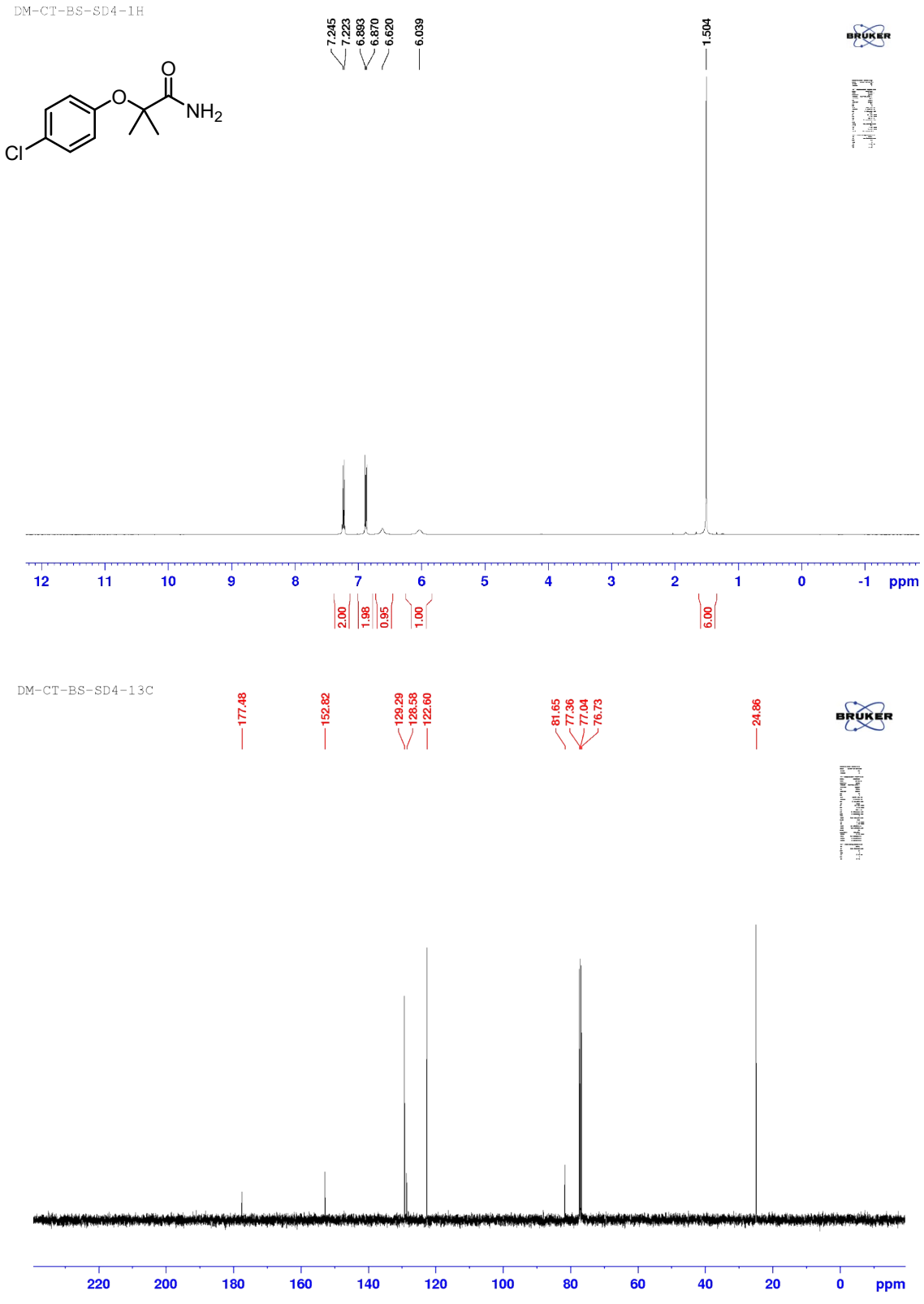
Supplementary Figure 12. ^{1}H NMR and ^{13}C NMR spectrum of furan-2-carboxamide **2j**



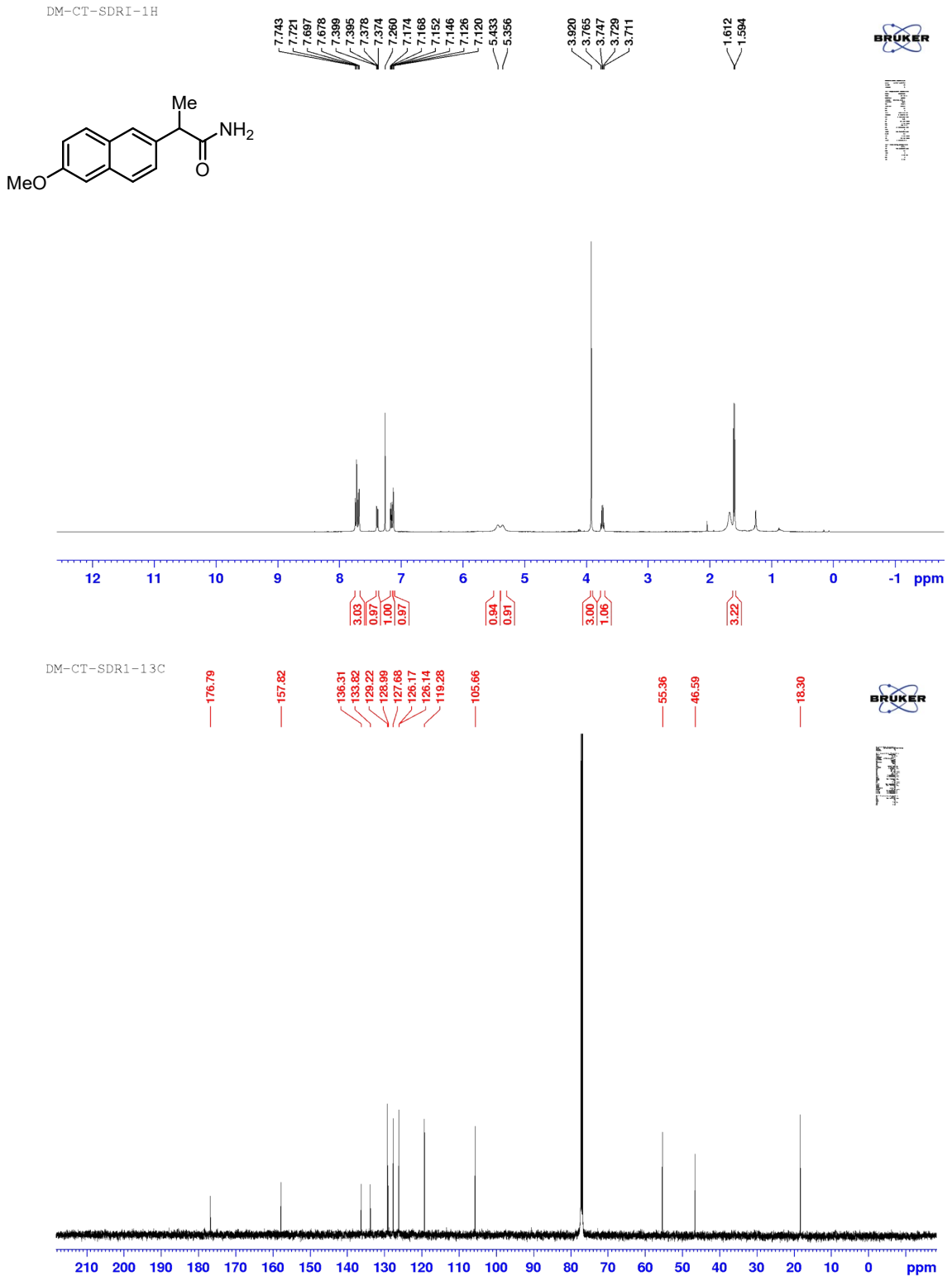
Supplementary Figure 13. ^{1}H NMR and ^{13}C NMR spectrum of thiophene-2-carboxamide **2k**



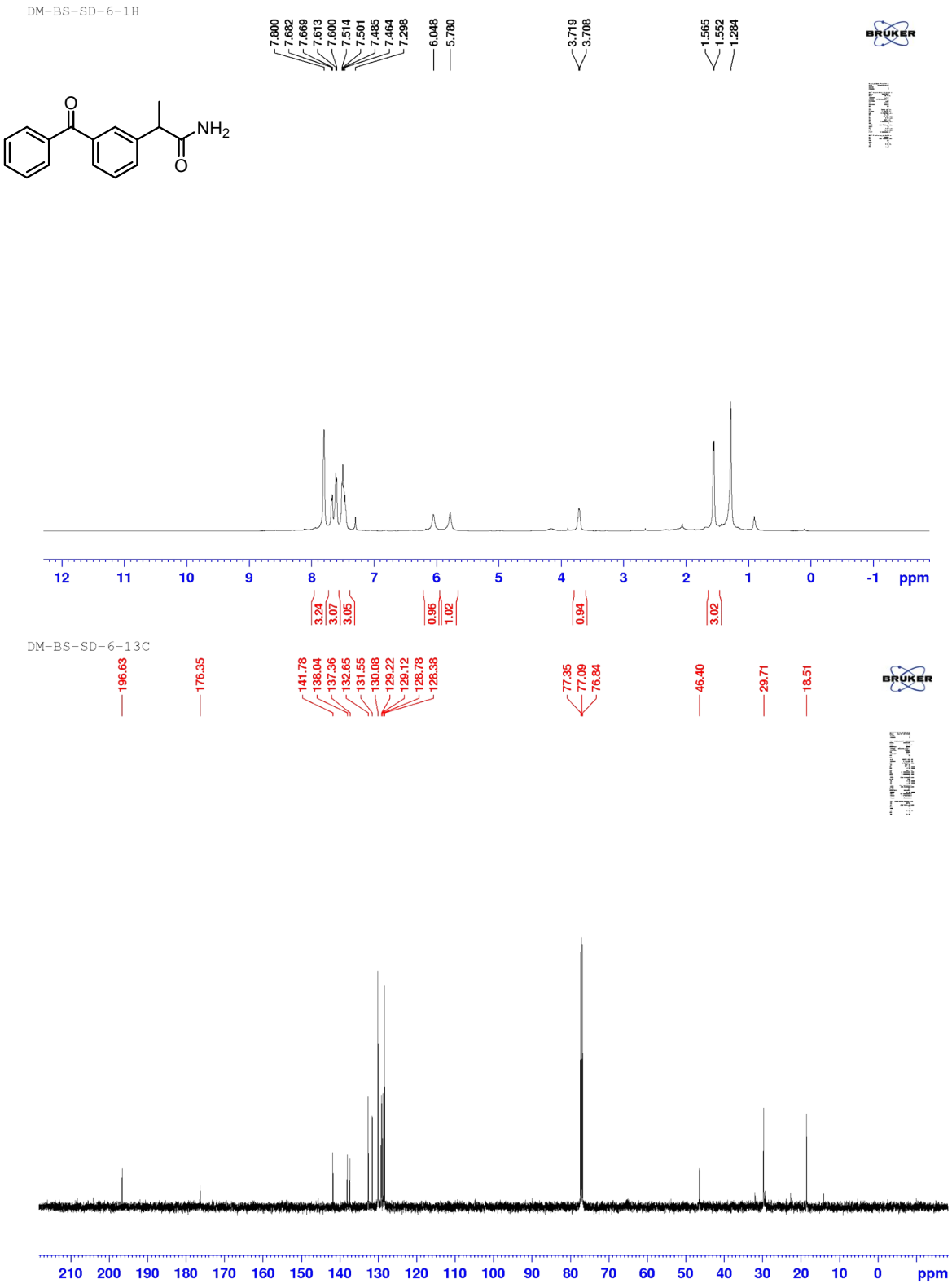
Supplementary Figure 14. ^{1}H NMR and ^{13}C NMR spectrum of nicotinamide **2l**



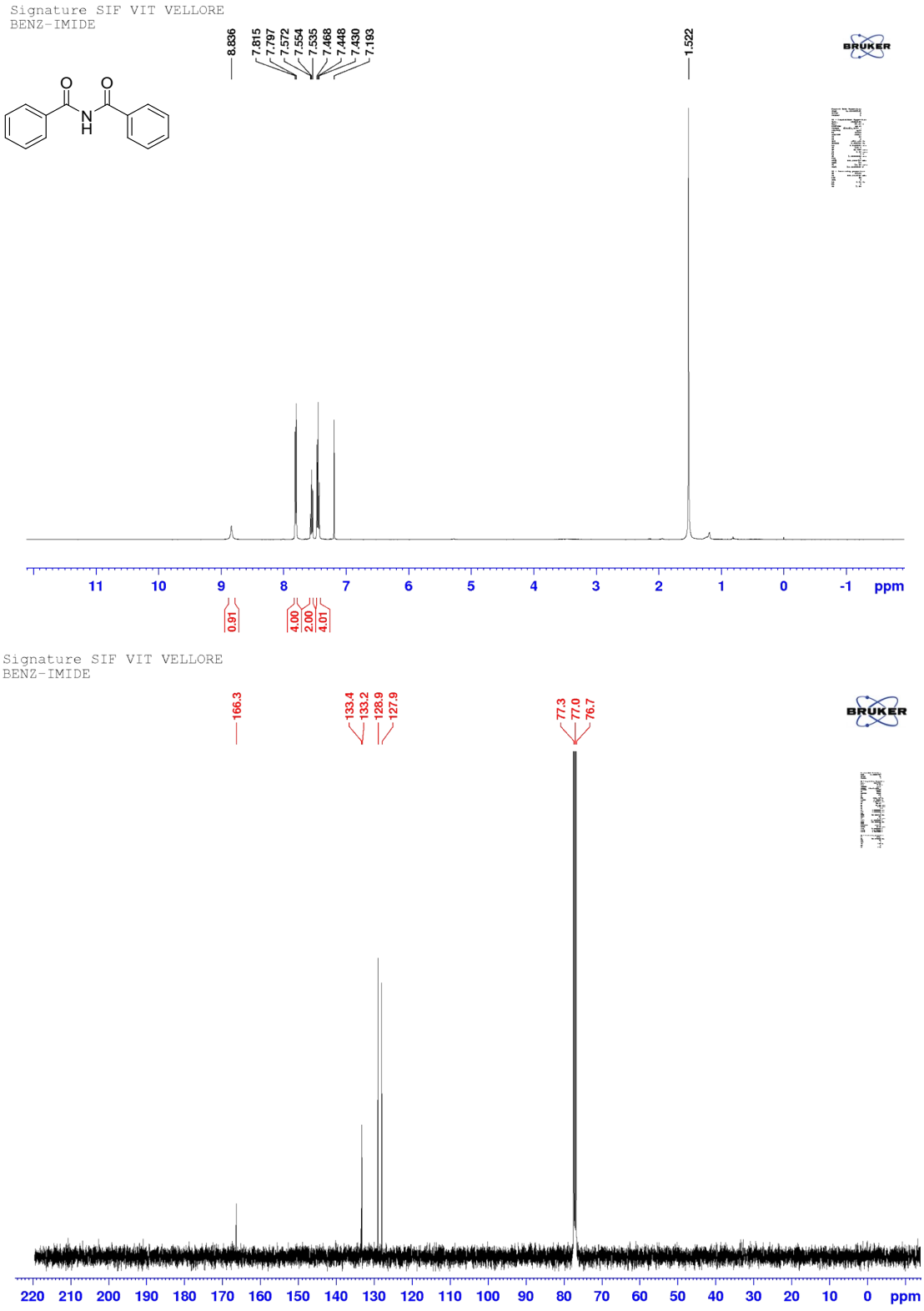
Supplementary Figure 15. ^{1}H NMR and ^{13}C NMR spectrum of 2-(4-chlorophenoxy)-2-methylpropanamide **2p**



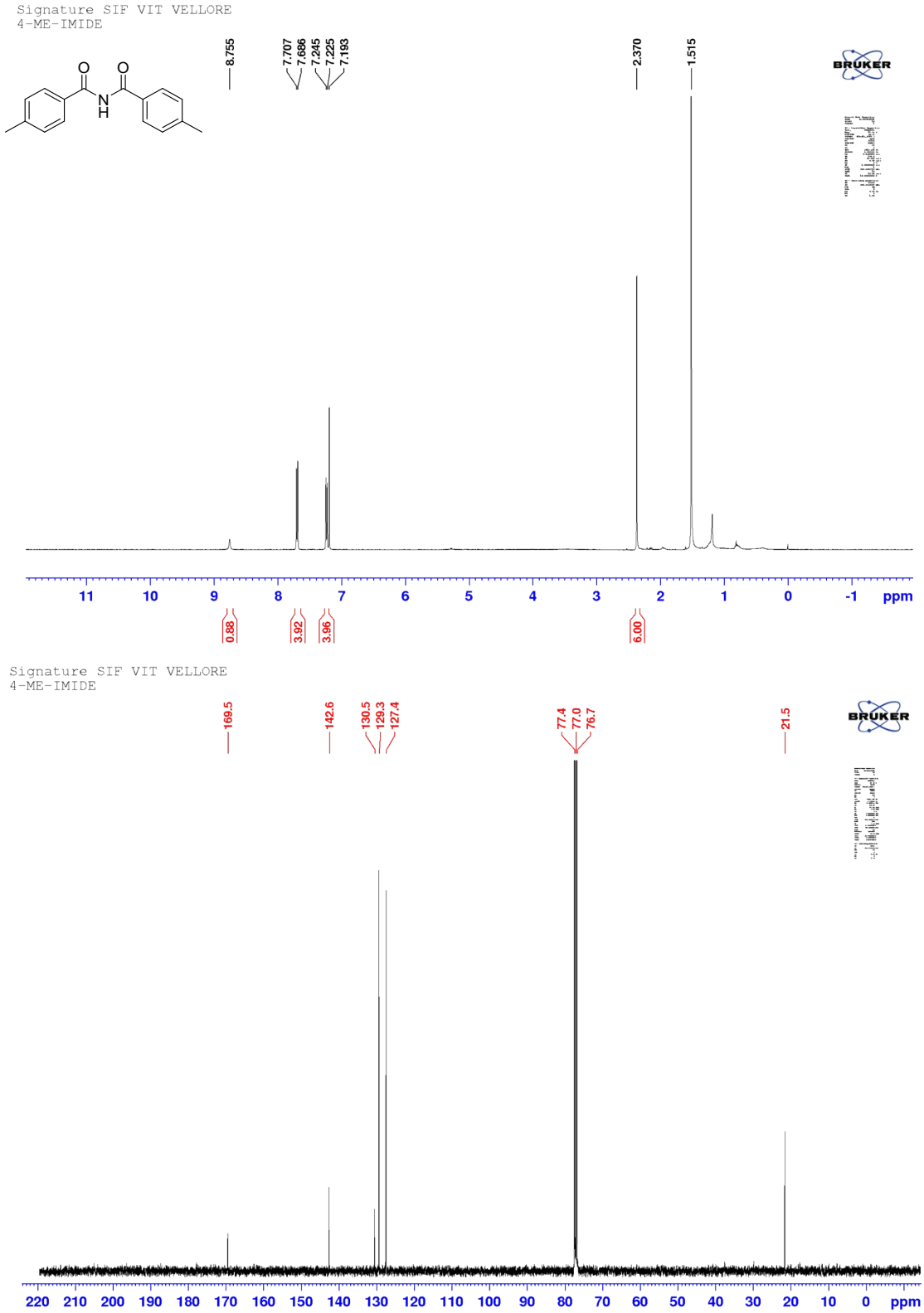
Supplementary Figure 16. ^{1}H NMR and ^{13}C NMR spectrum of 2-(6-methoxynaphthalen-2-yl)propenamide **2q**



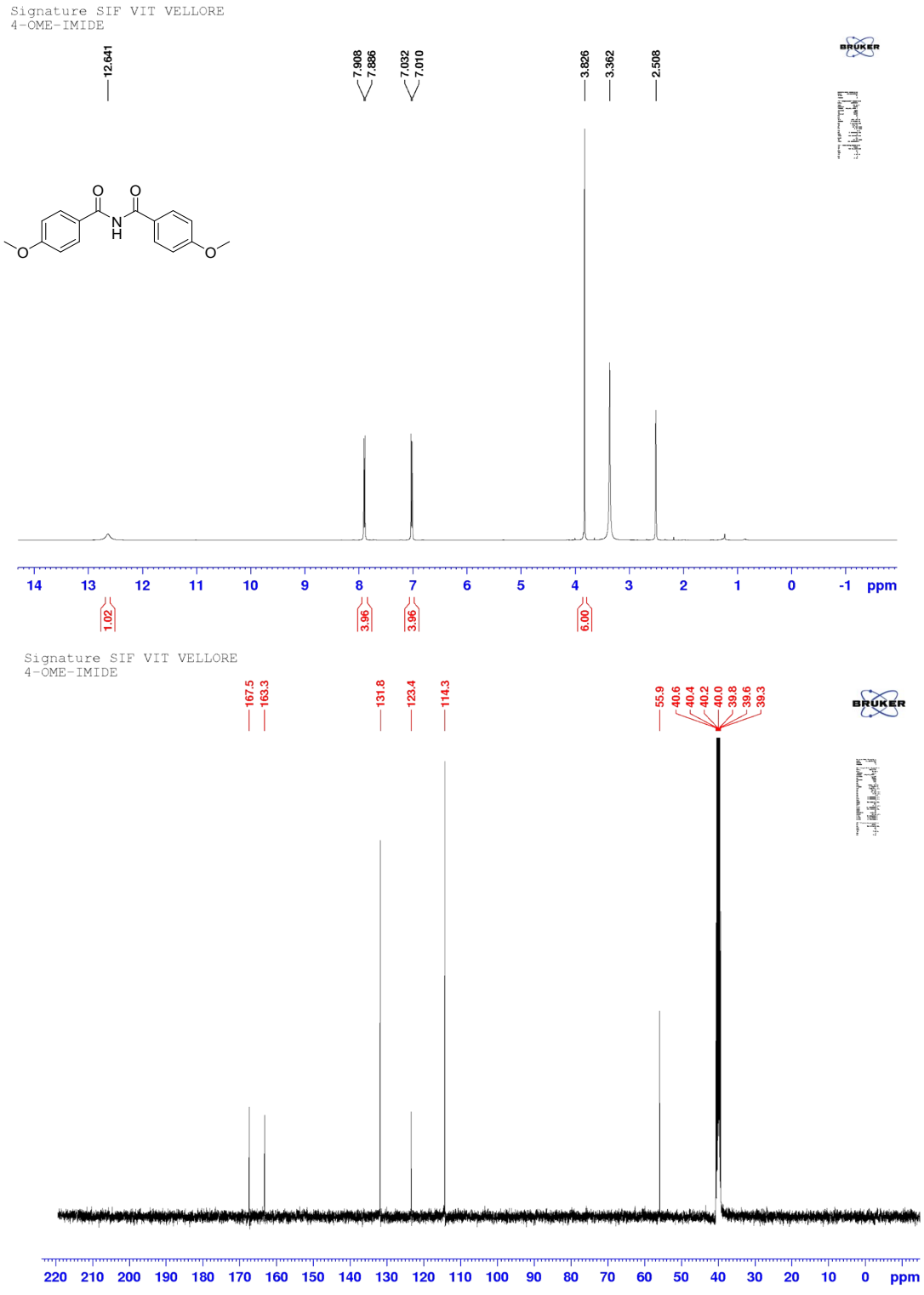
Supplementary Figure 17. ^{1}H NMR and ^{13}C NMR spectrum of 2-(3-benzoylphenyl)propenamide **2r**



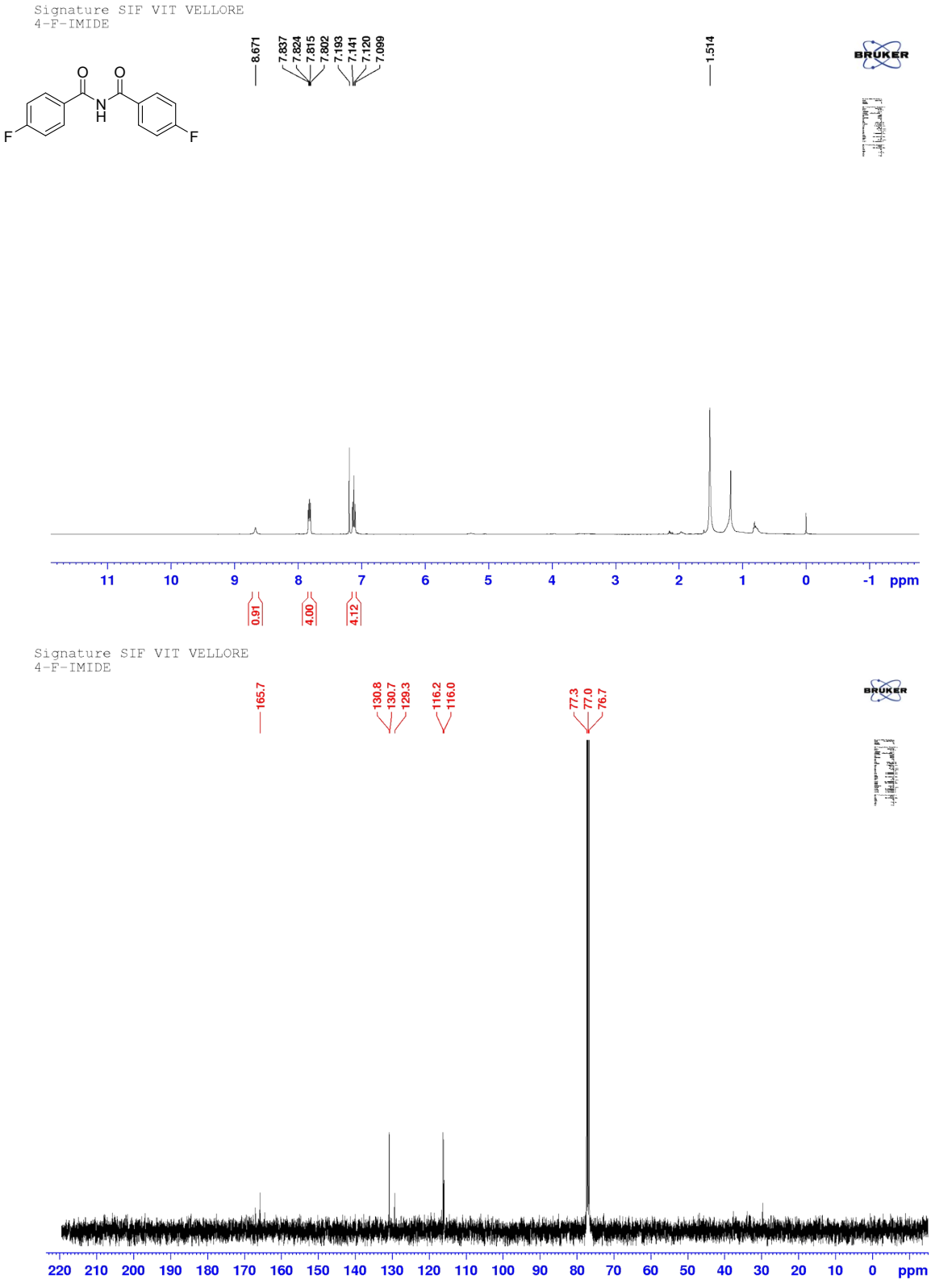
Supplementary Figure 18. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoylbenzamide **3a**



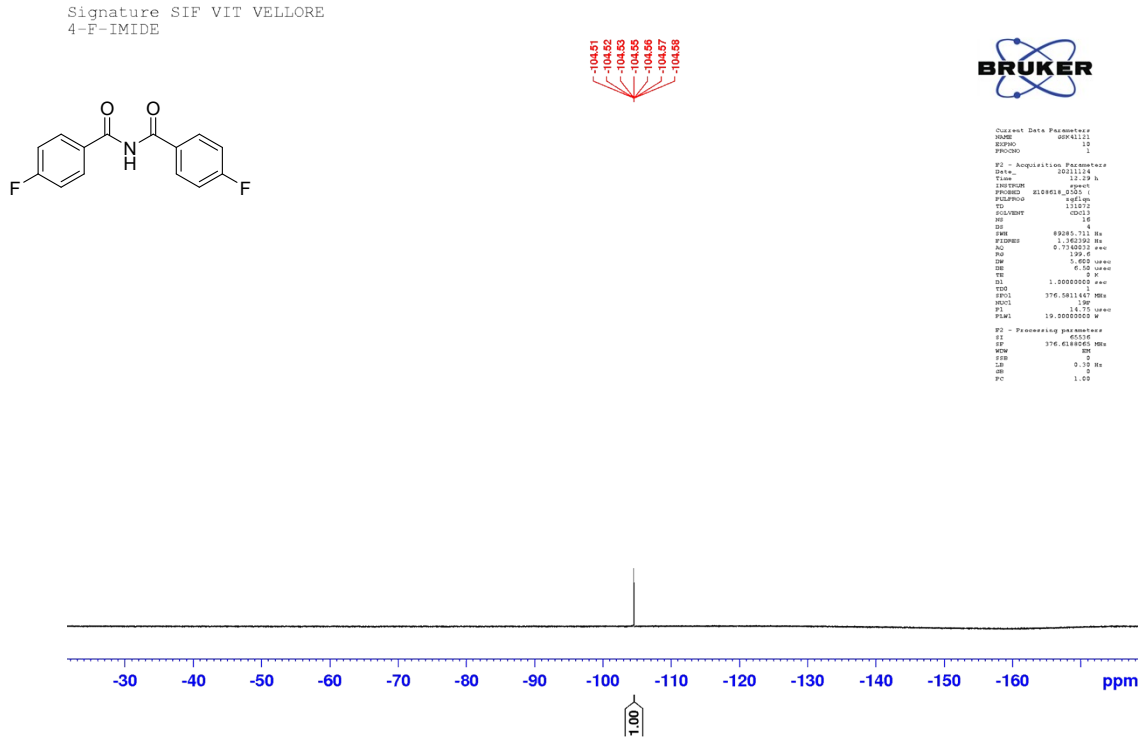
Supplementary Figure 19. ^{1}H NMR and ^{13}C NMR spectrum of 4-methyl-*N*-(4-methylbenzoyl)benzamide **3b**



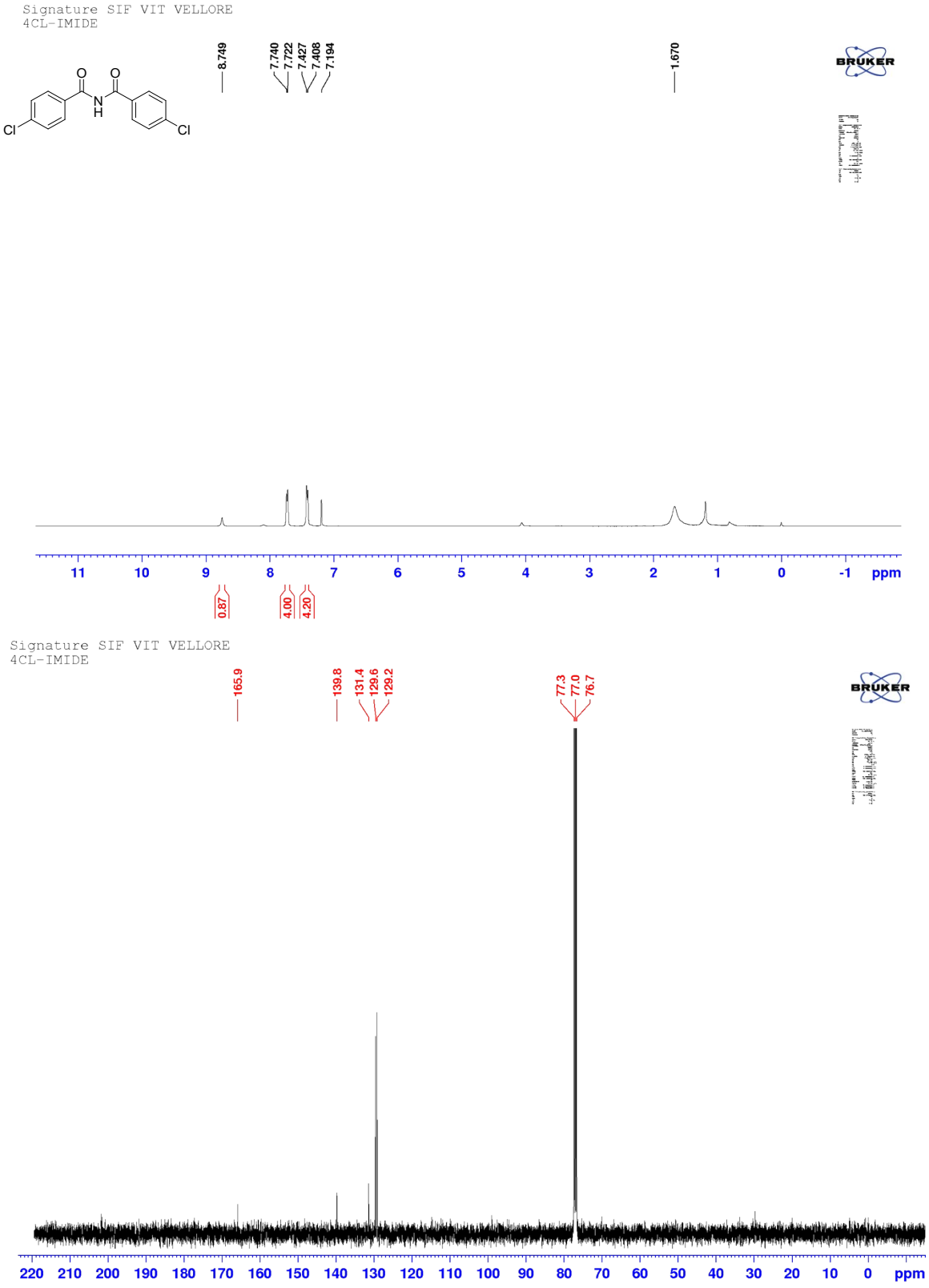
Supplementary Figure 20. ^{1}H NMR and ^{13}C NMR spectrum of 4-methoxy-*N*-(4-methoxybenzoyl)benzamide **3c**



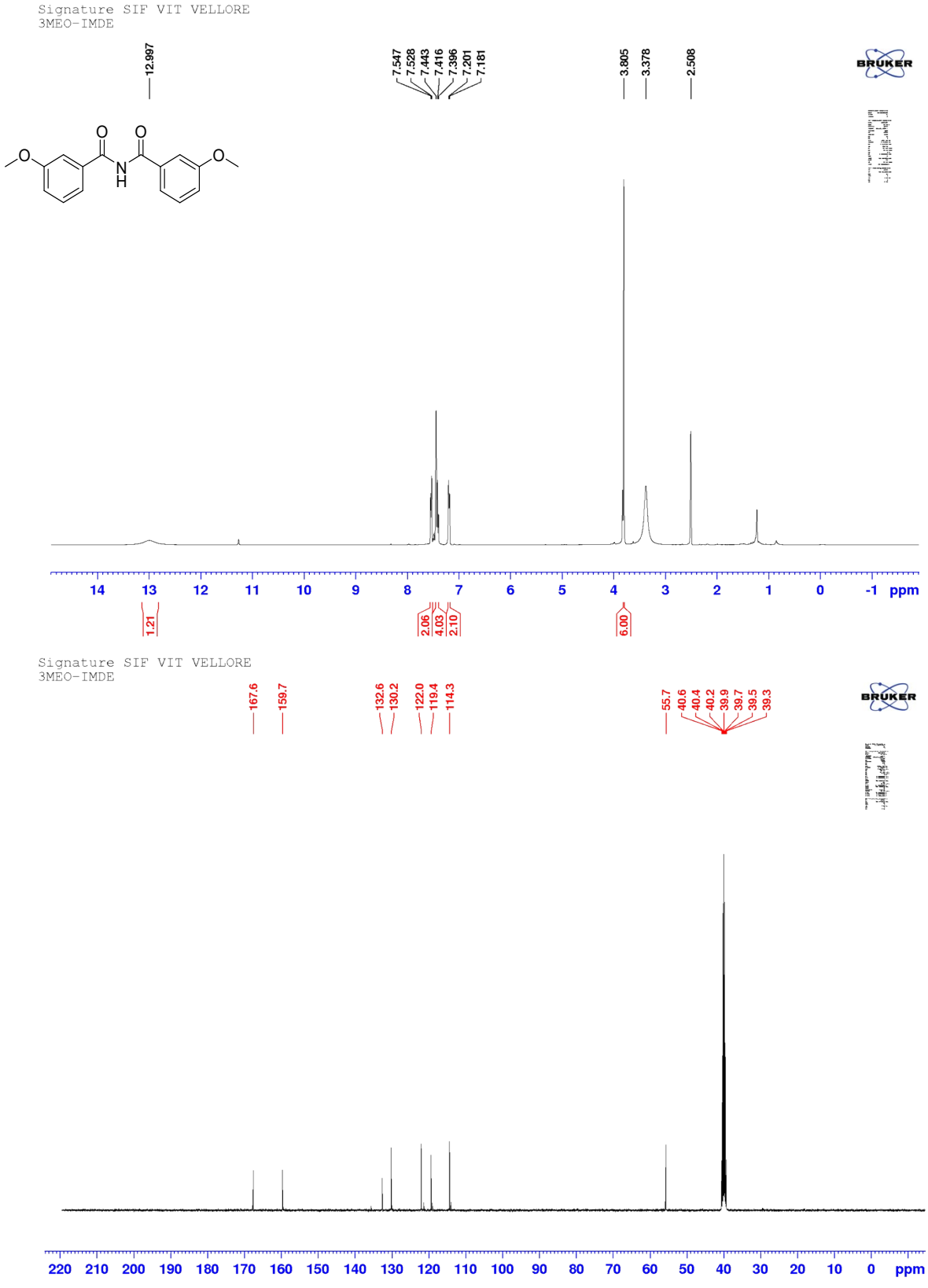
Supplementary Figure 21. ^{1}H NMR and ^{13}C NMR spectrum of 4-fluoro-*N*-(4-fluorobenzoyl)benzamide **3d**



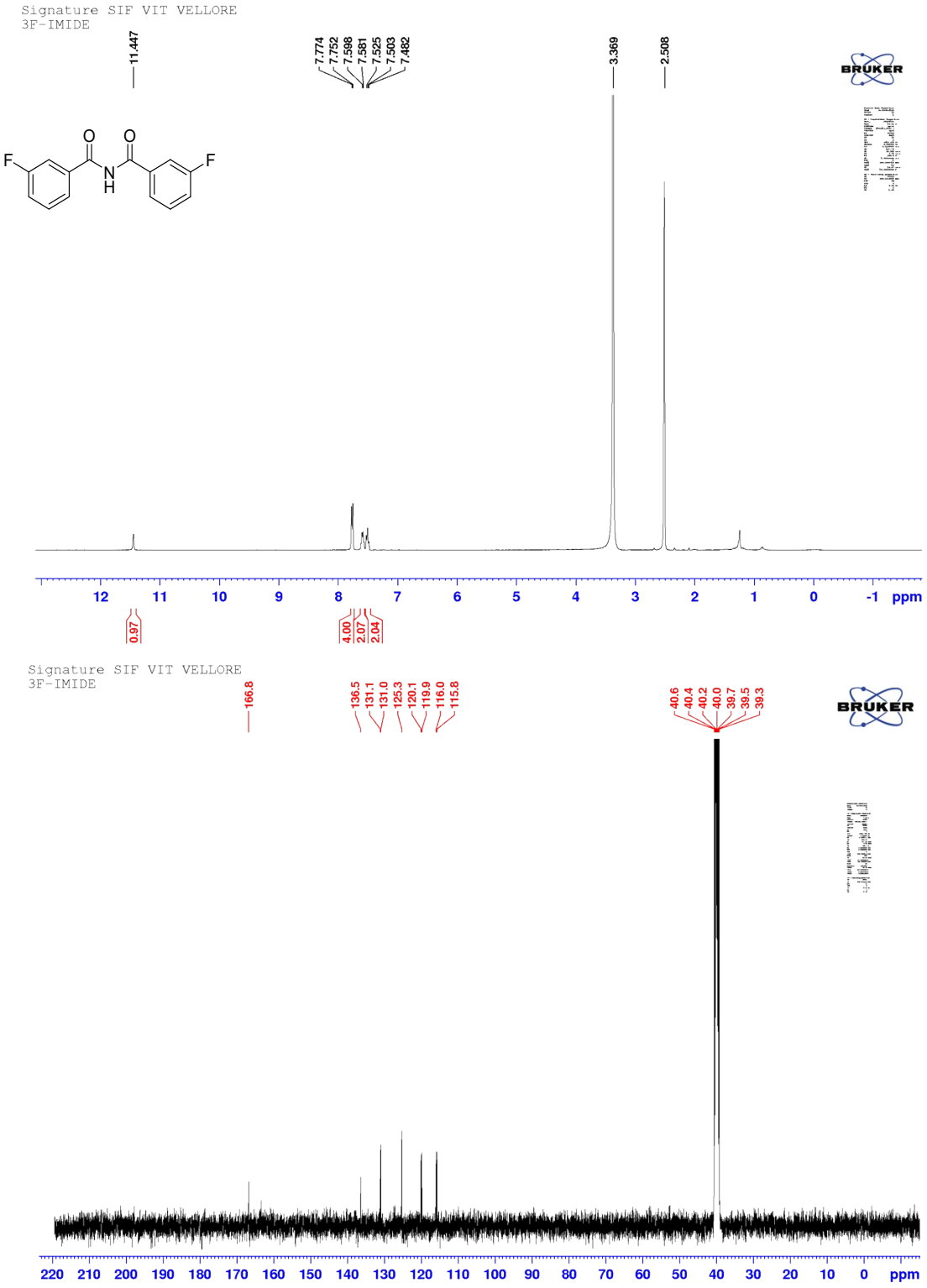
Supplementary Figure 22. ^{19}F NMR spectrum of 4-fluoro-*N*-(4-fluorobenzoyl)benzamide **3d**



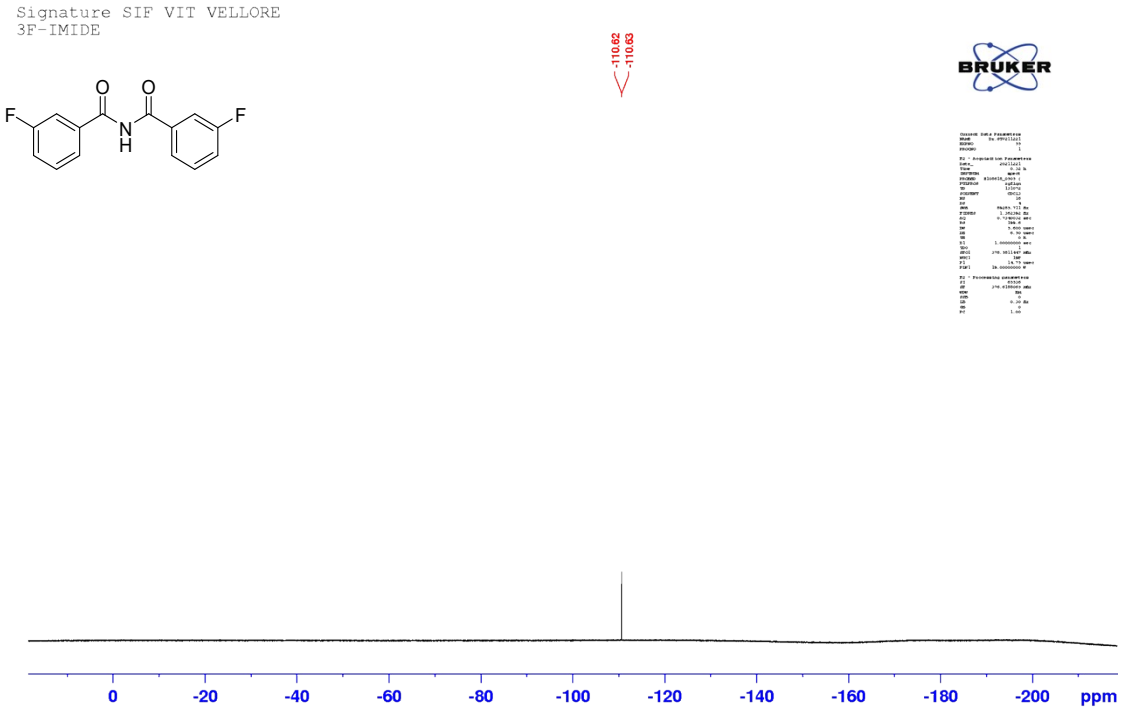
Supplementary Figure 23. ^{1}H NMR and ^{13}C NMR spectrum of 4-chloro-*N*-(4-chlorobenzoyl)benzamide **3e**



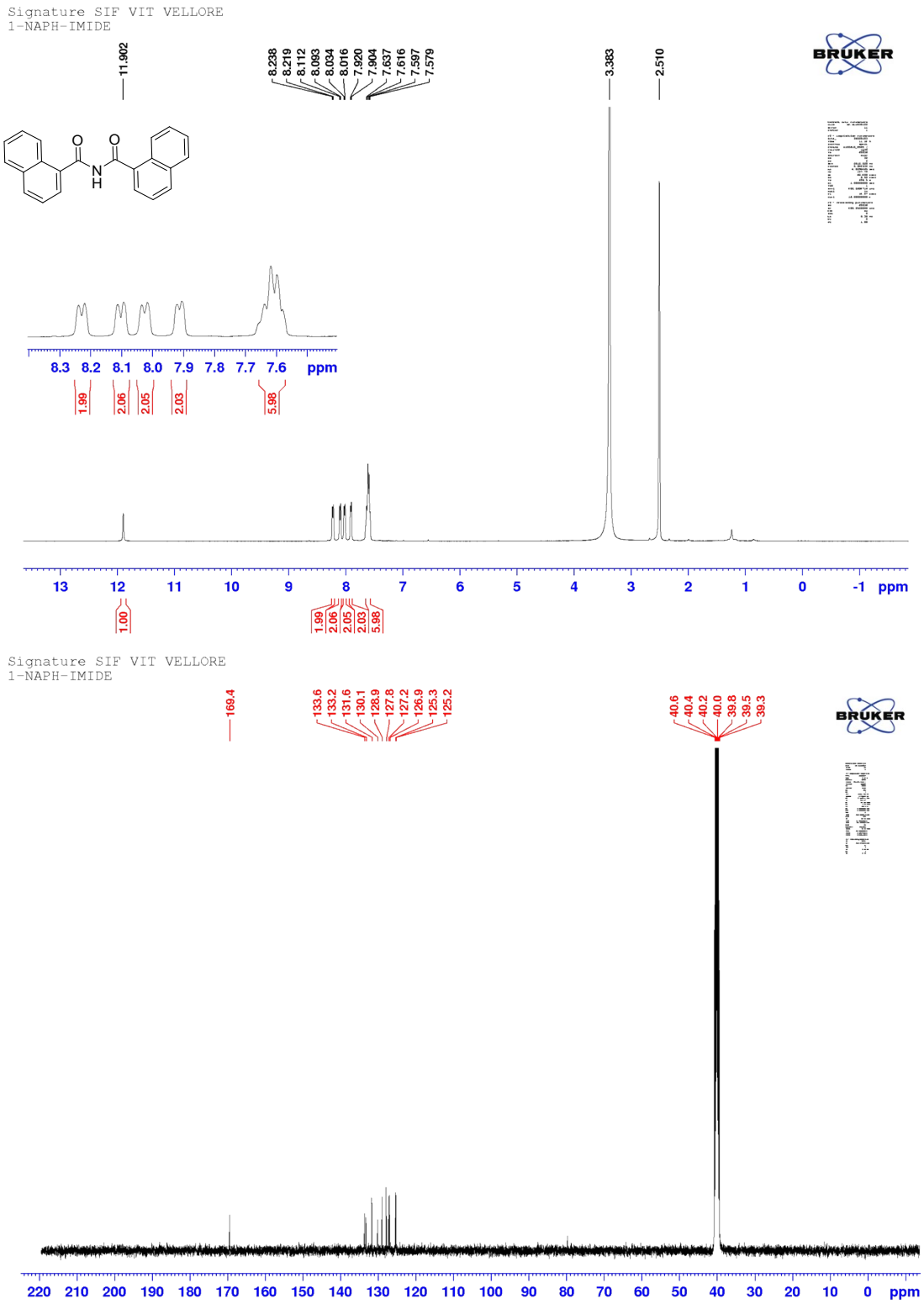
Supplementary Figure 24. ^{1}H NMR and ^{13}C NMR spectrum of 3-methoxy-*N*-(3-methoxybenzoyl)benzamide **3f**



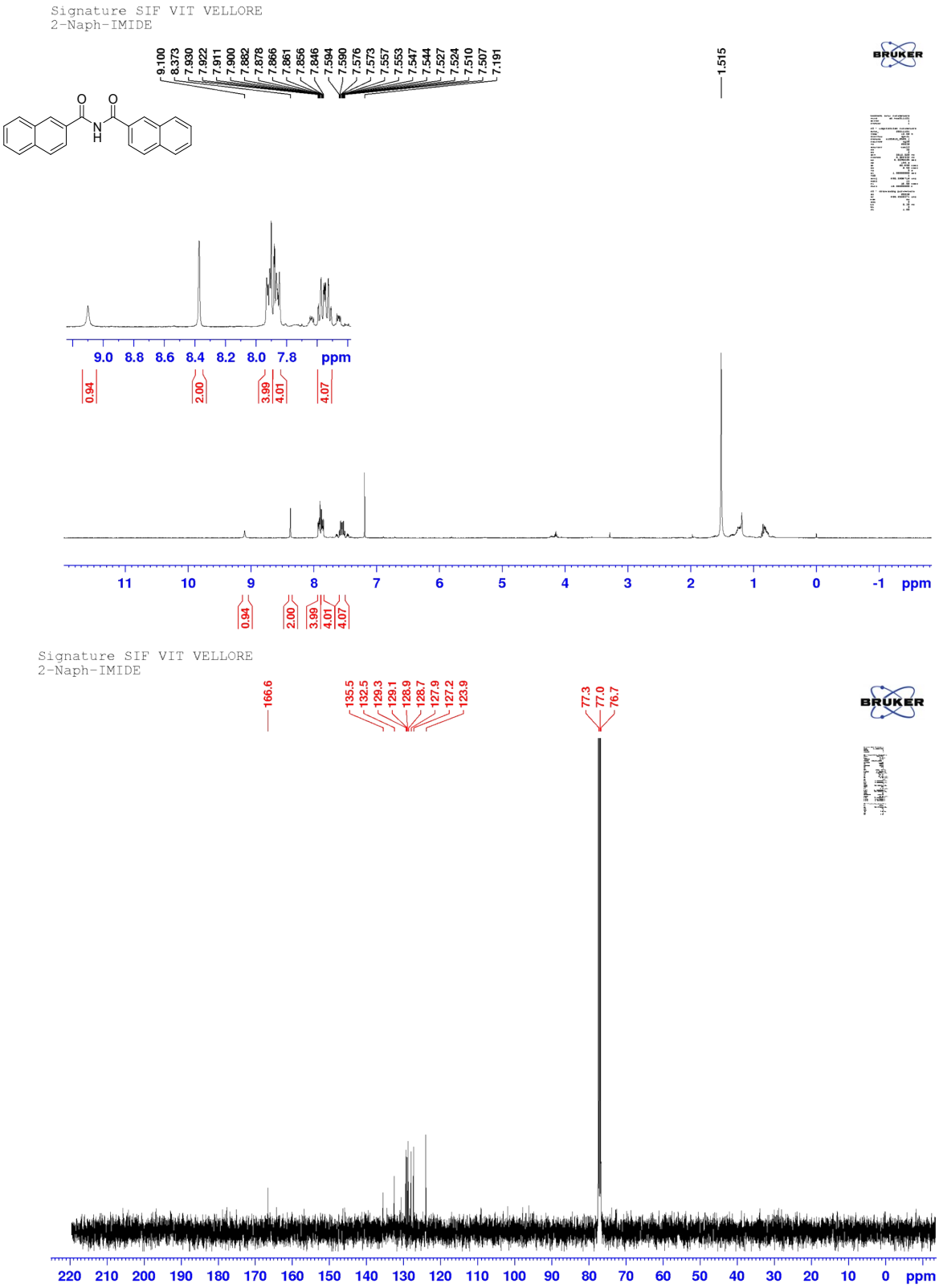
Supplementary Figure 25. ^{1}H NMR and ^{13}C NMR spectrum of 3-fluoro-*N*-(3-fluorobenzoyl)benzamide **3g**



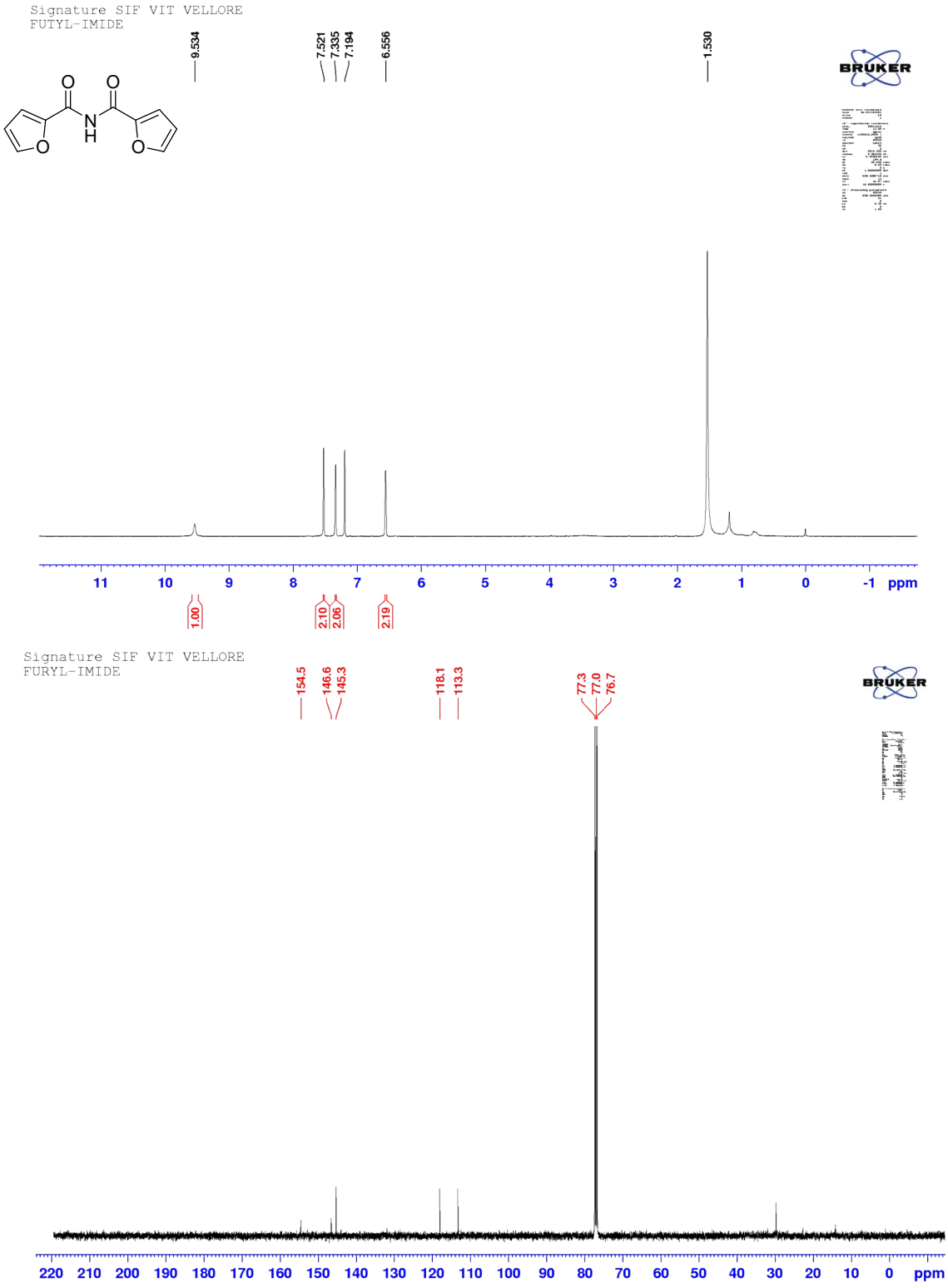
Supplementary Figure 26. ^{19}F NMR spectrum of 3-fluoro-*N*-(3-fluorobenzoyl)benzamide **3g**



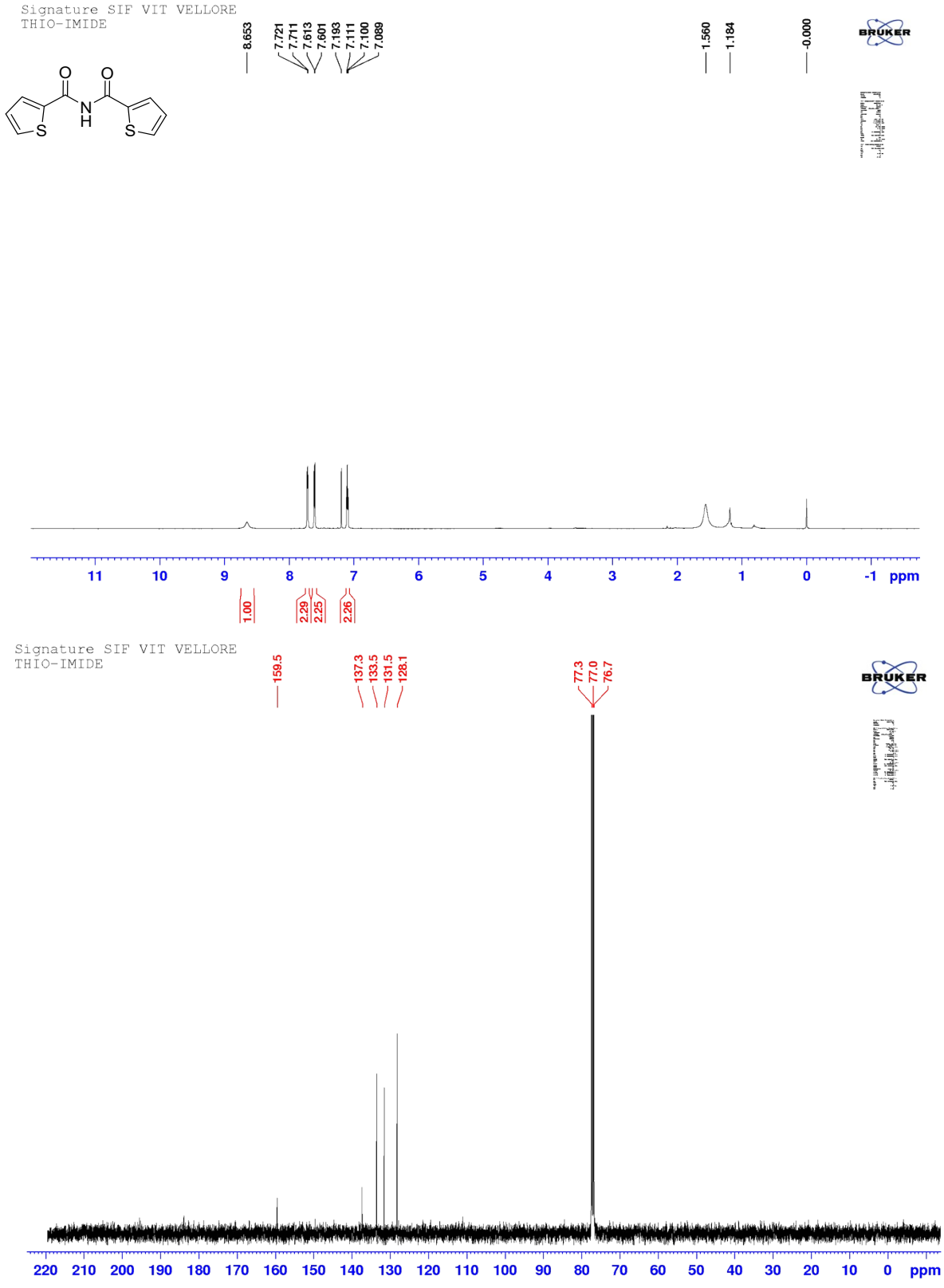
Supplementary Figure 27. ^{1}H NMR and ^{13}C NMR spectrum of *N*-(1-naphthoyl)-1-naphthamide **3h**



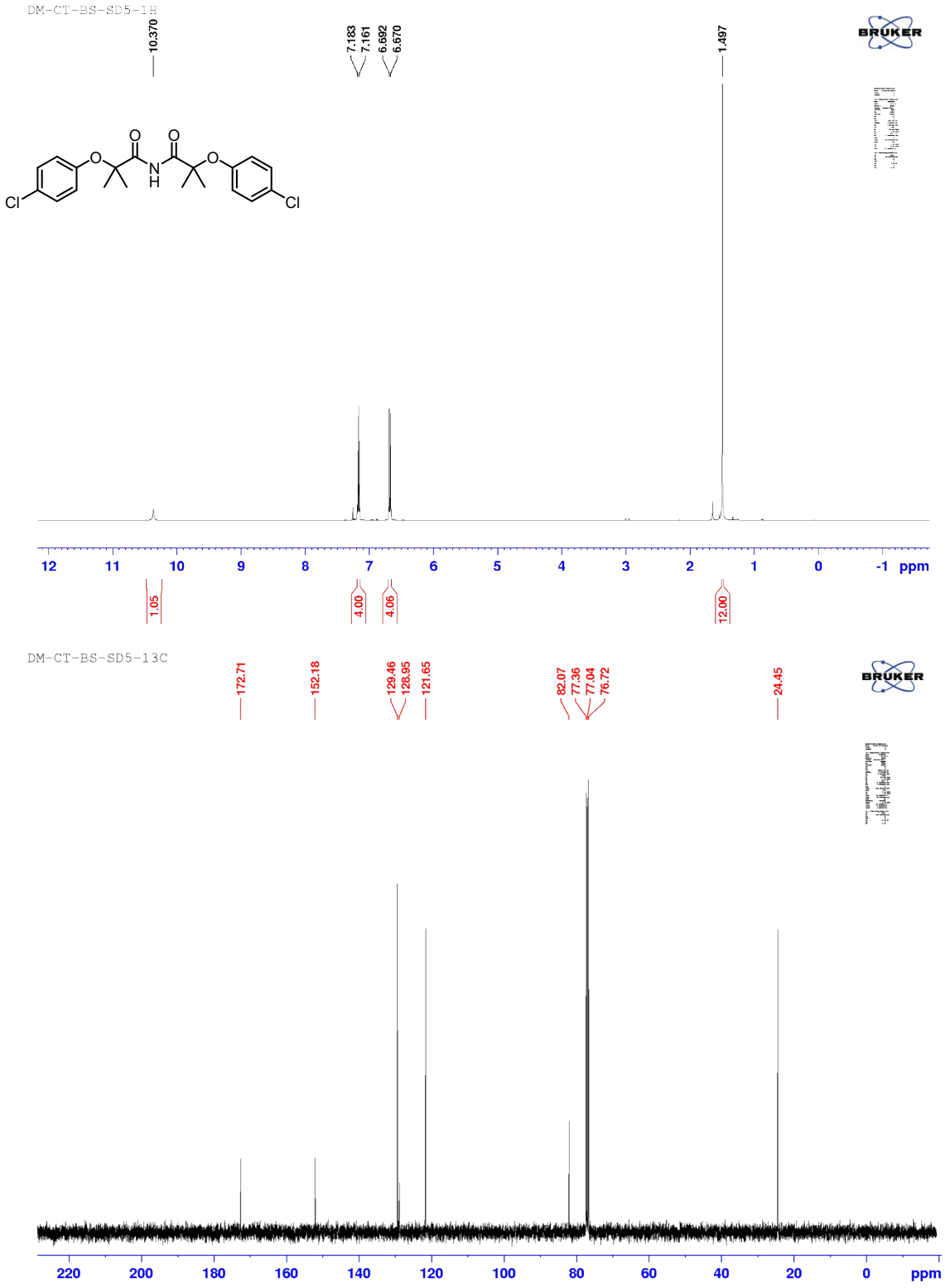
Supplementary Figure 28. ^{1}H NMR and ^{13}C NMR spectrum of *N*-(2-naphthoyl)-2-naphthamide **3i**



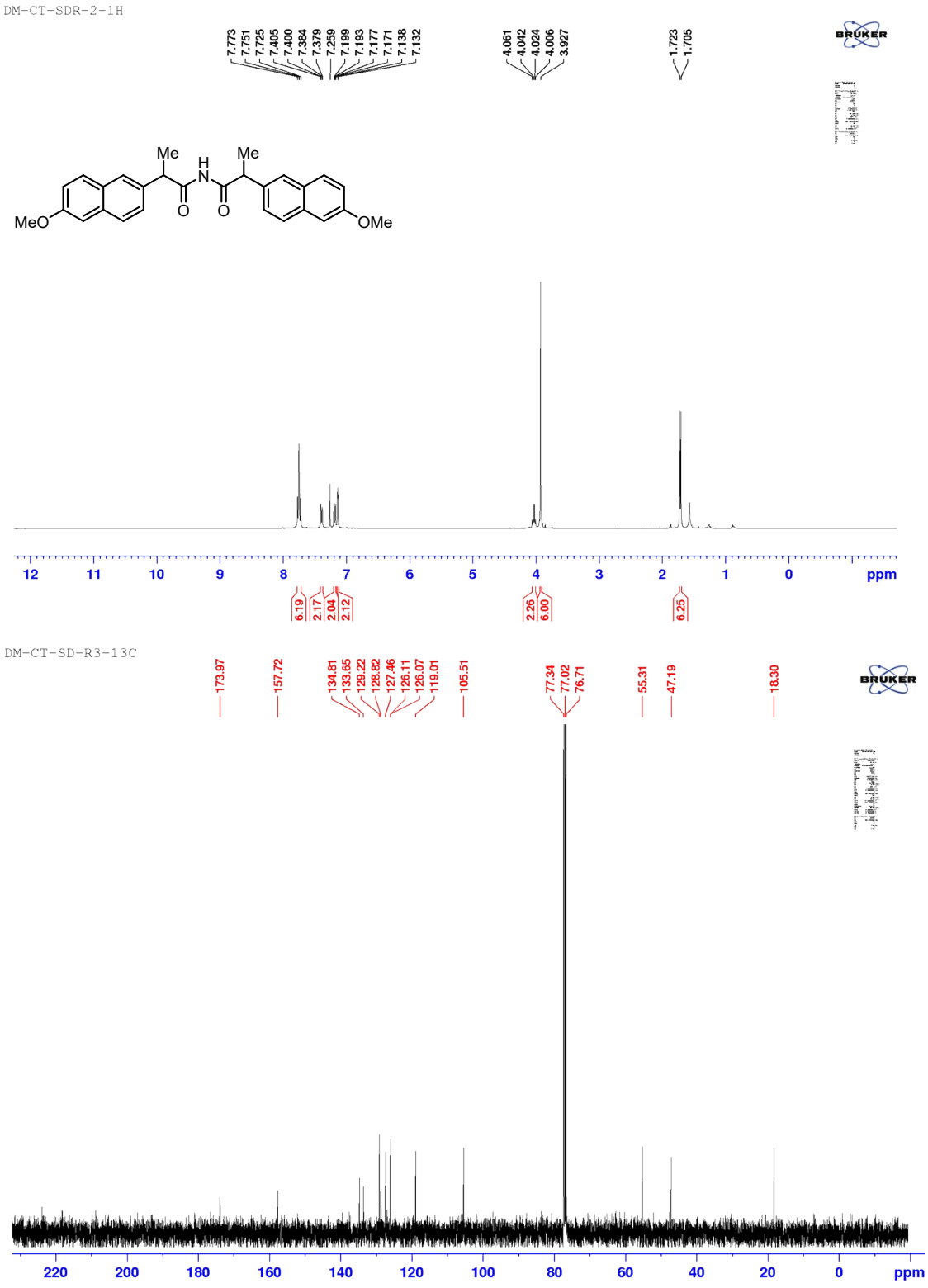
Supplementary Figure 29. ^{1}H NMR and ^{13}C NMR spectrum of *N*-(furan-2-carbonyl)furan-2-carboxamide **3j**



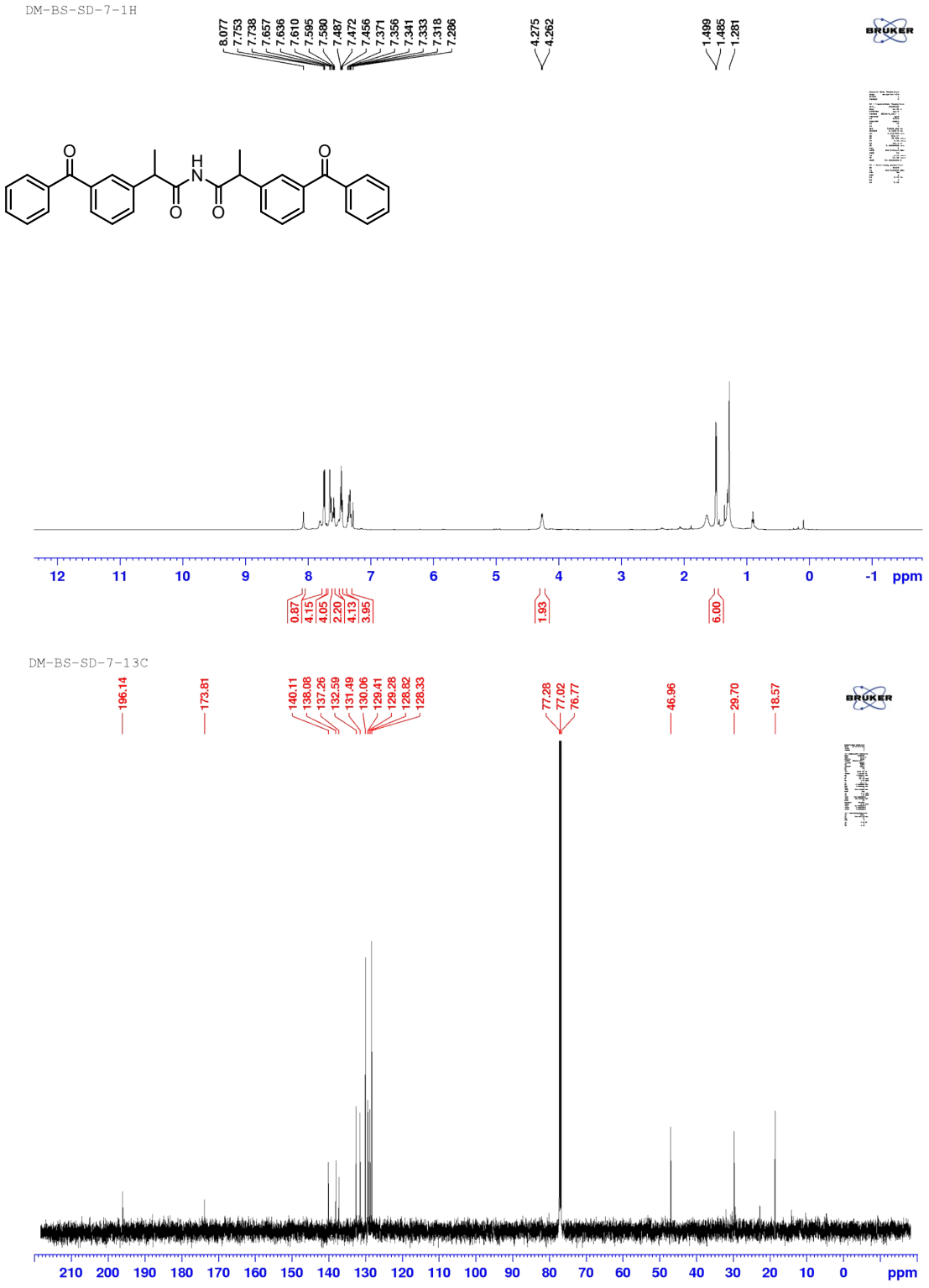
Supplementary Figure 30. ^{1}H NMR and ^{13}C NMR spectrum of *N*-(thiophene-2-carbonyl)thiophene-2-carboxamide **3k**



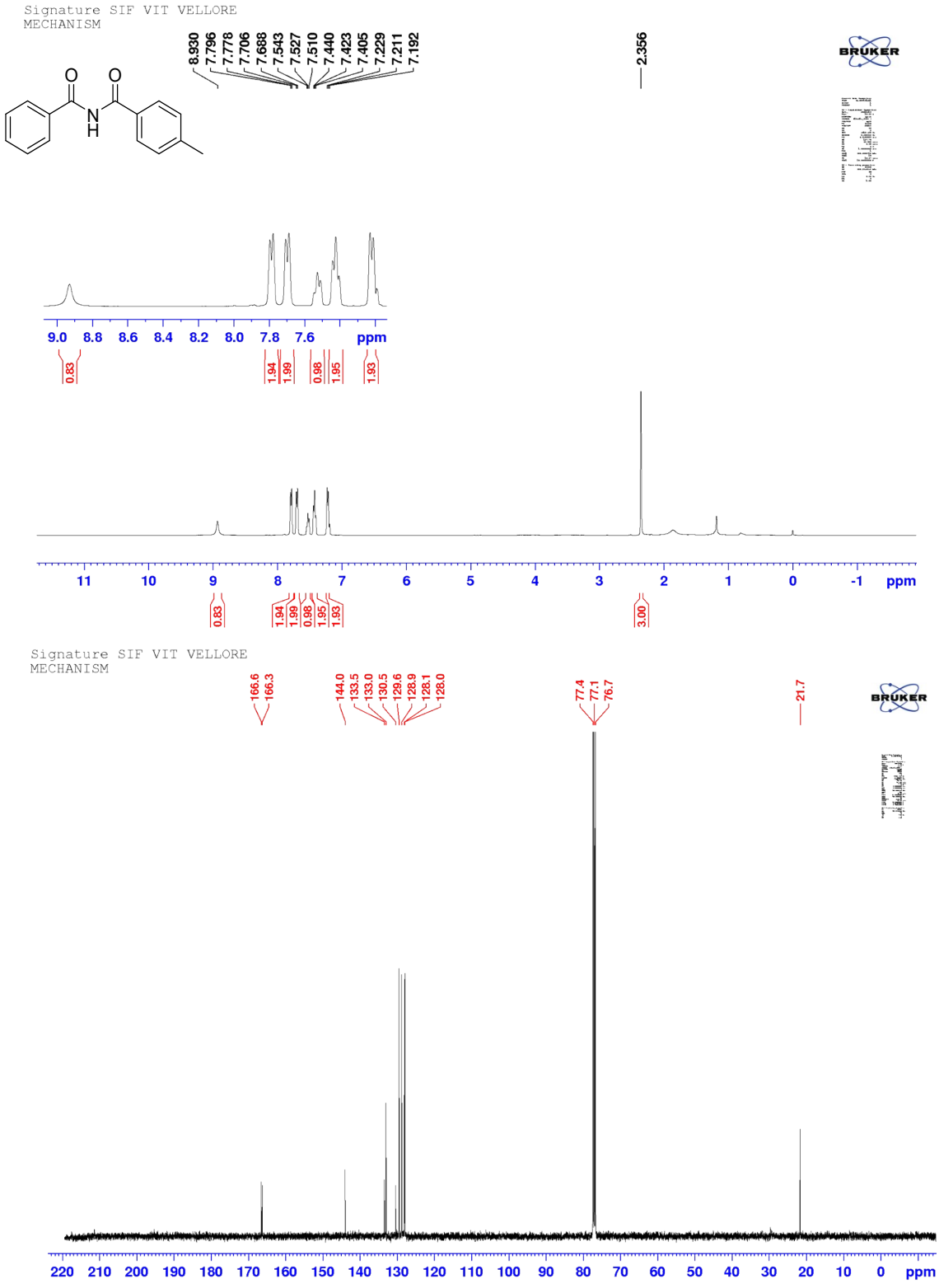
Supplementary Figure 31. ^{1}H NMR and ^{13}C NMR spectrum of 2-(4-chlorophenoxy)-N-(2-(4-chlorophenoxy)-2-methylpropanoyl)-2-methylpropanamide **3l**



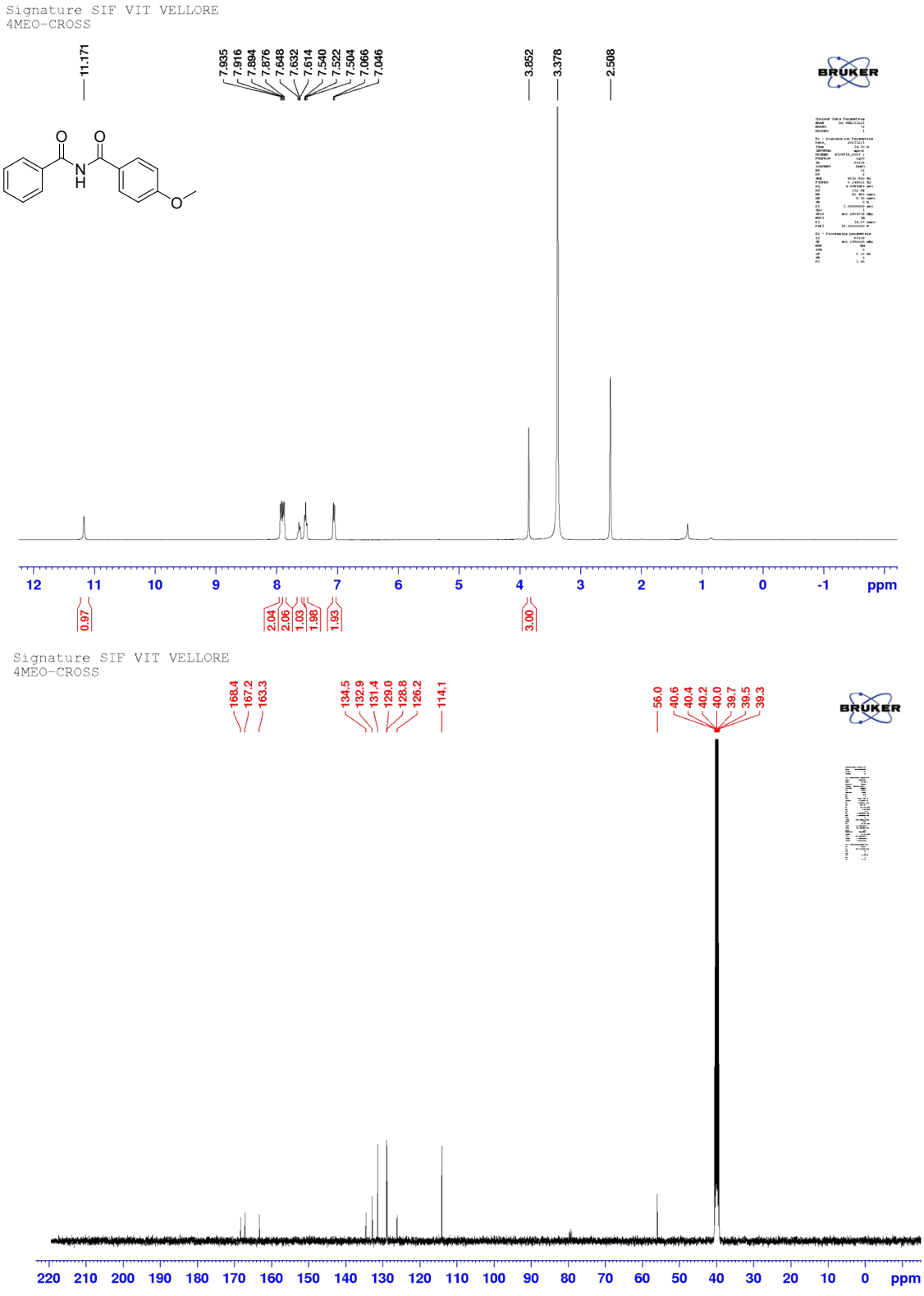
Supplementary Figure 32. ^{1}H NMR and ^{13}C NMR spectrum of 2-(6-methoxynaphthalen-2-yl)-N-(2-(6-methoxynaphthalen-2-yl)propanoyl)propenamide **3m**



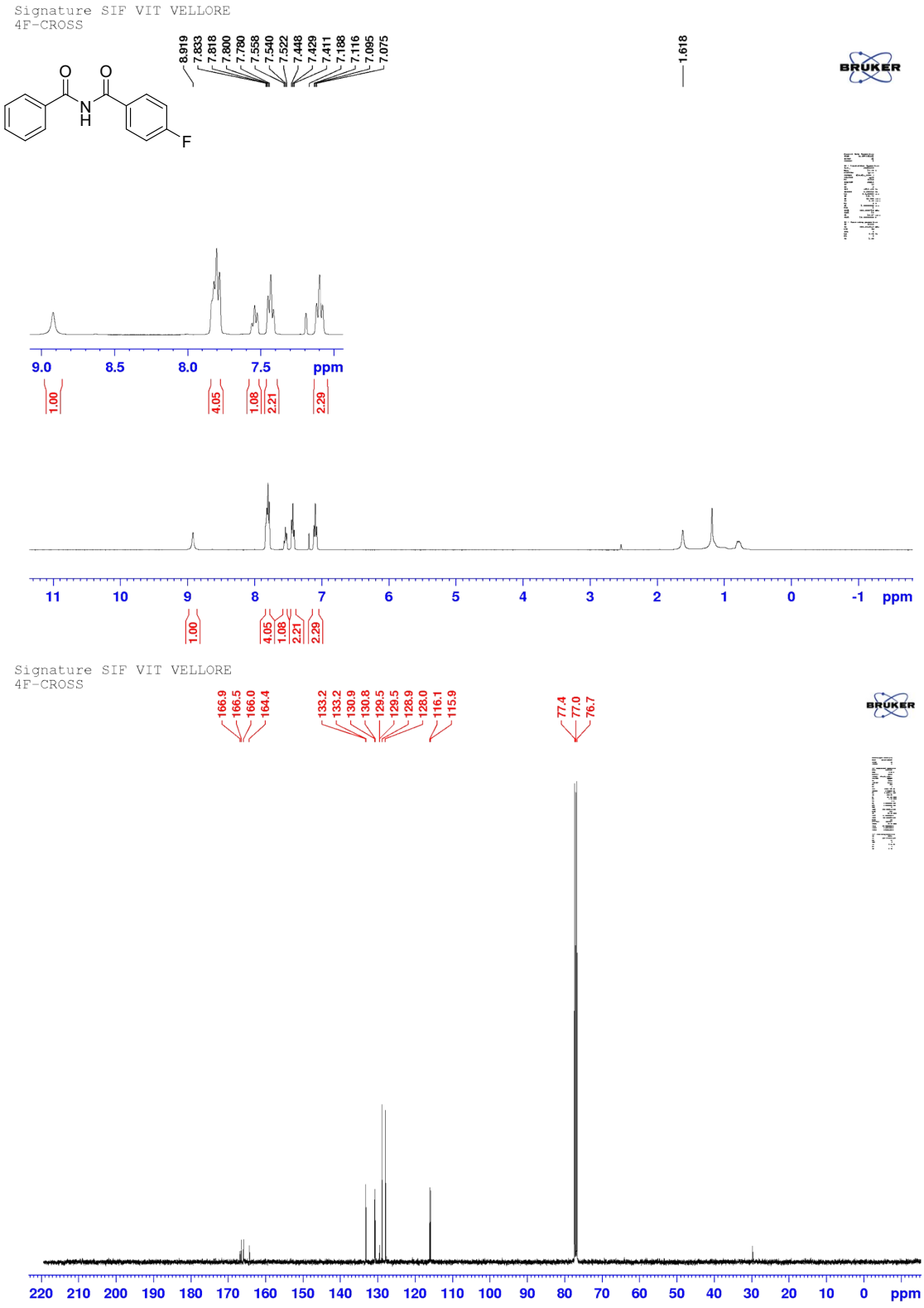
Supplementary Figure 33. ^{1}H NMR and ^{13}C NMR spectrum of 2-(3-benzoylphenyl)-N-(2-(3-benzoylphenyl)propanoyl)propenamide **3n**



Supplementary Figure 34. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-4-methylbenzamide **4a**

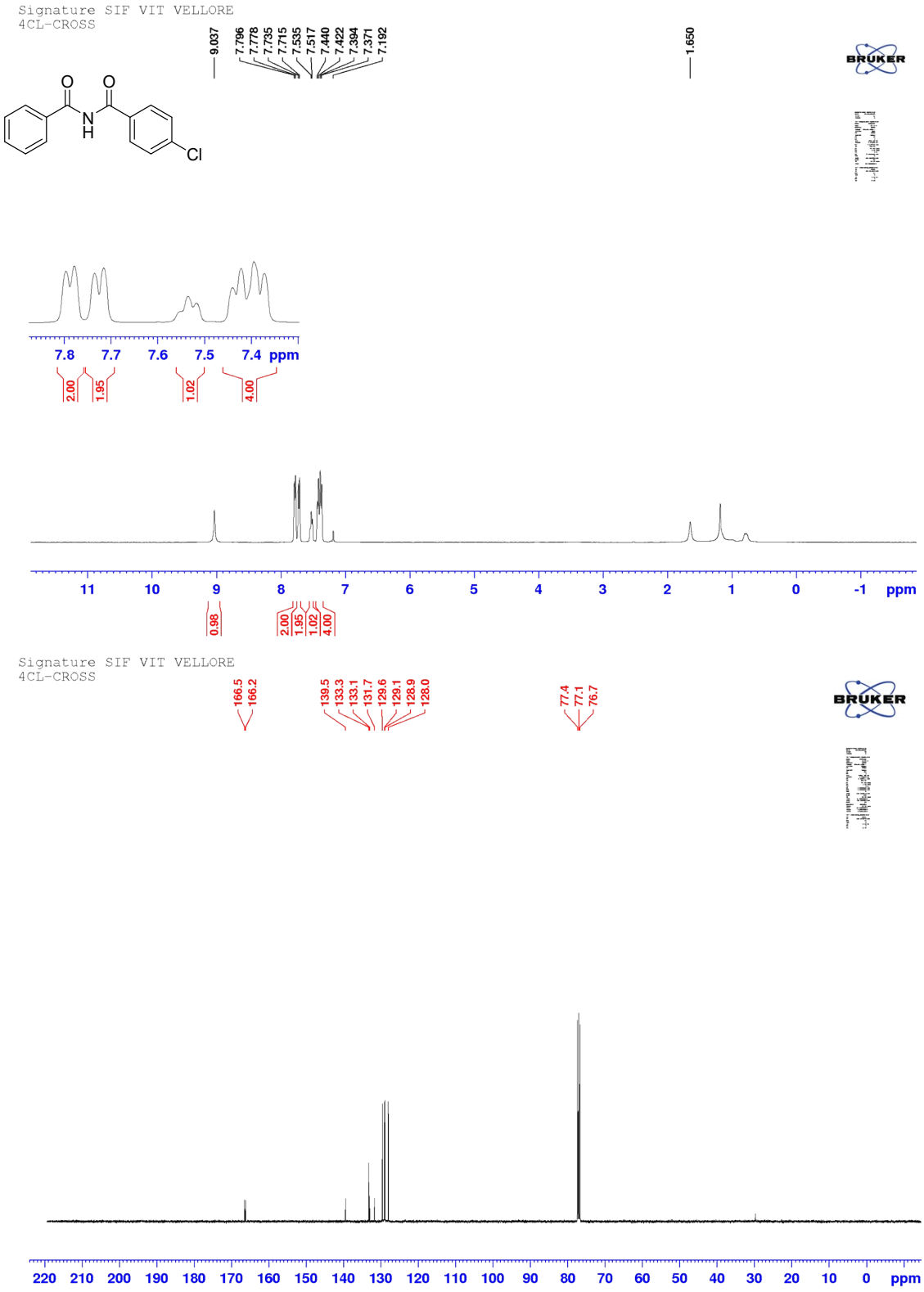


Supplementary Figure 35. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-4-methoxybenzamide **4b**

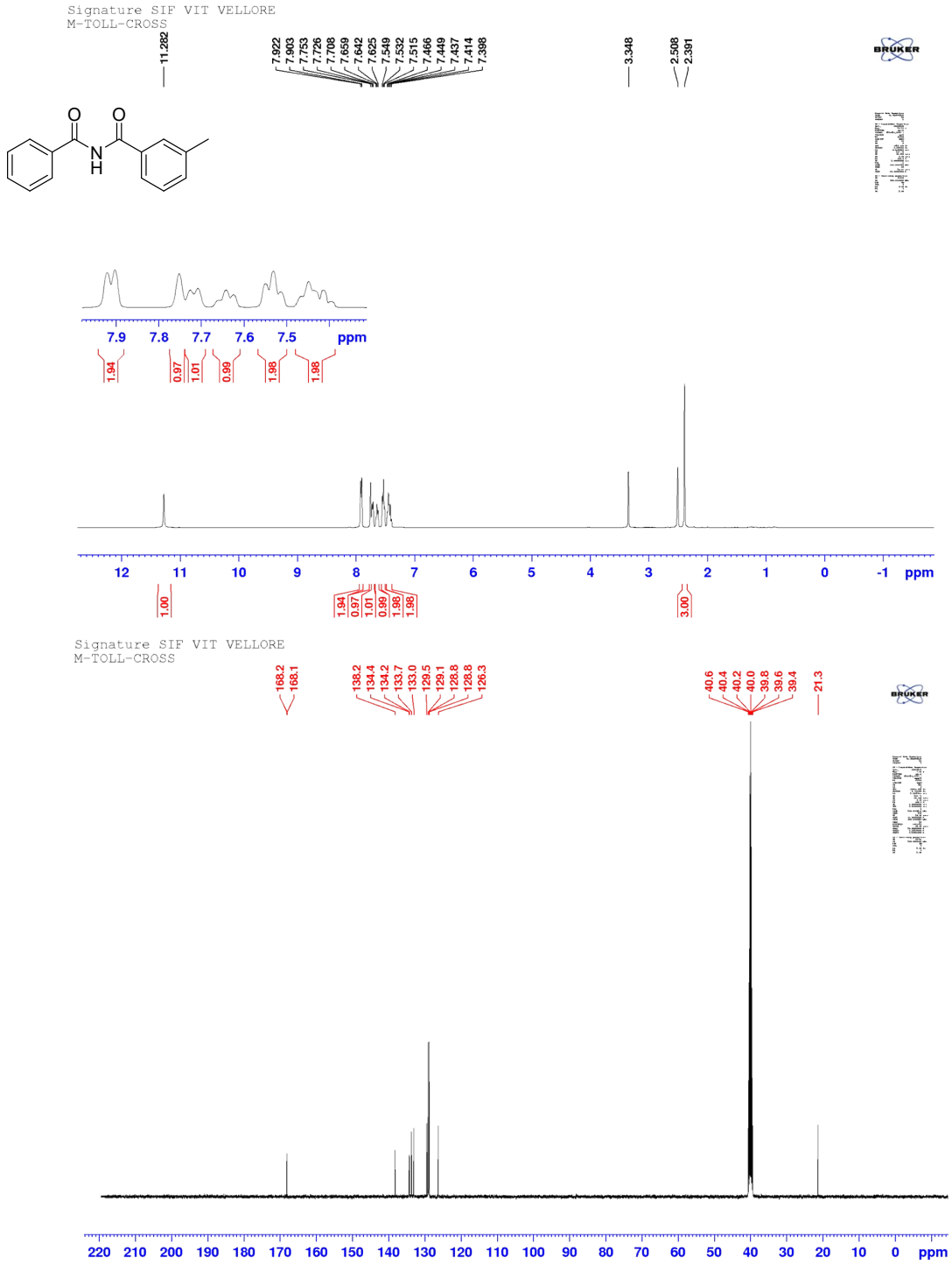


Supplementary Figure 36. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-4-fluorobenzamide **4c**

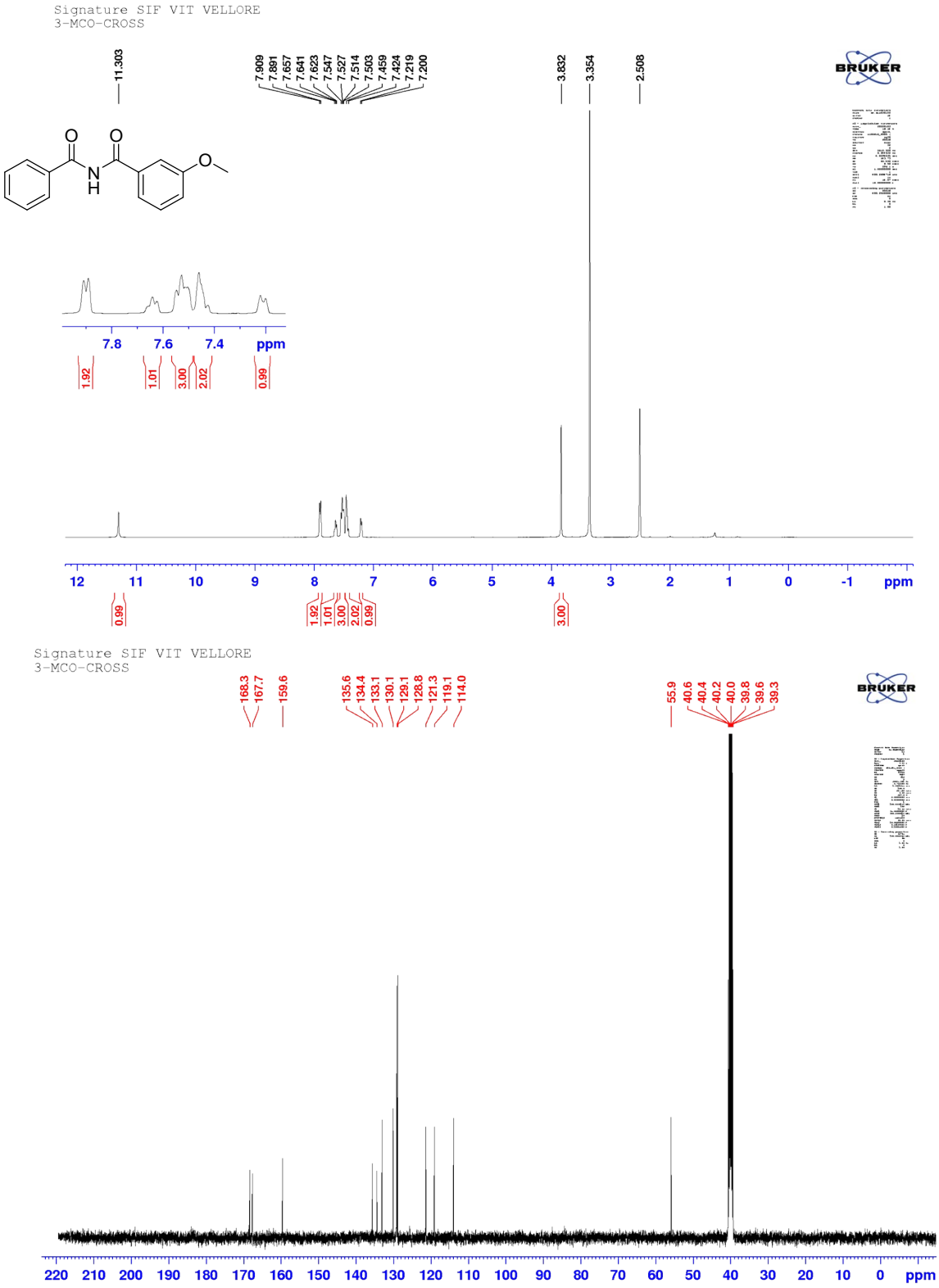
Supplementary Figure 37. ^{19}F NMR spectrum of *N*-benzoyl-4-fluorobenzamide **4c**



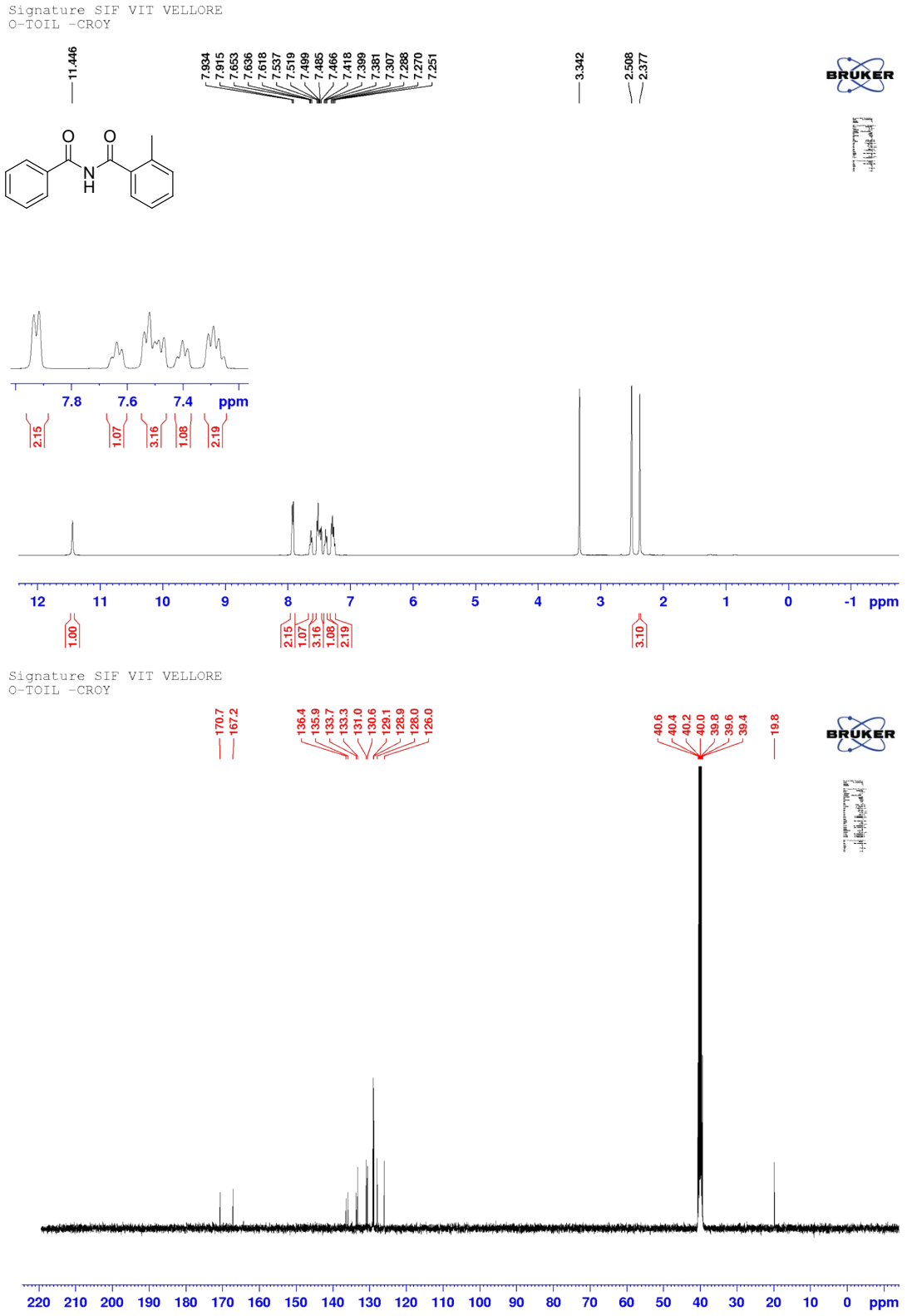
Supplementary Figure 38. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-4-chlorobenzamide **4d**



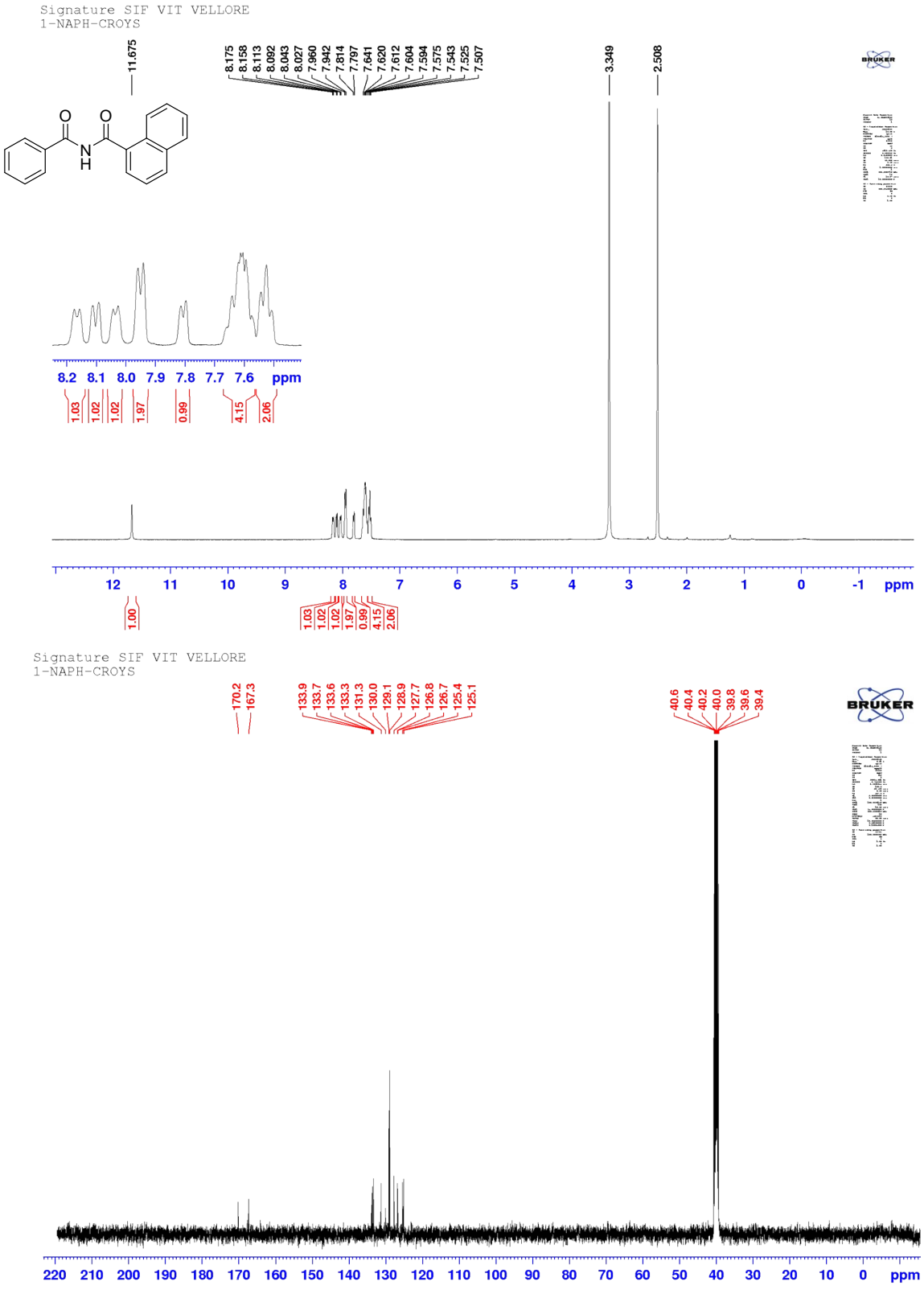
Supplementary Figure 39. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-3-methylbenzamide **4e**



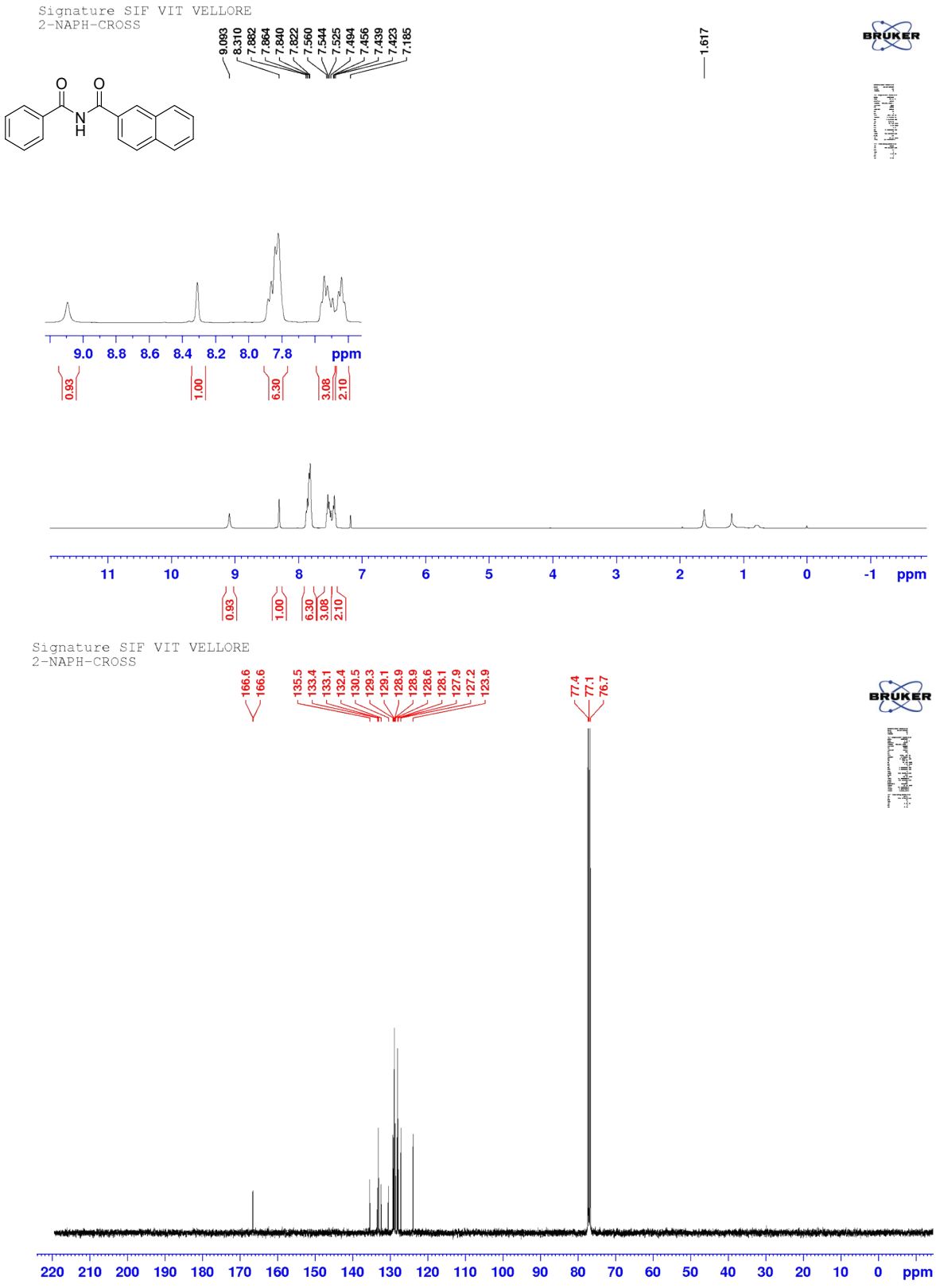
Supplementary Figure 40. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-3-methoxybenzamide **4f**



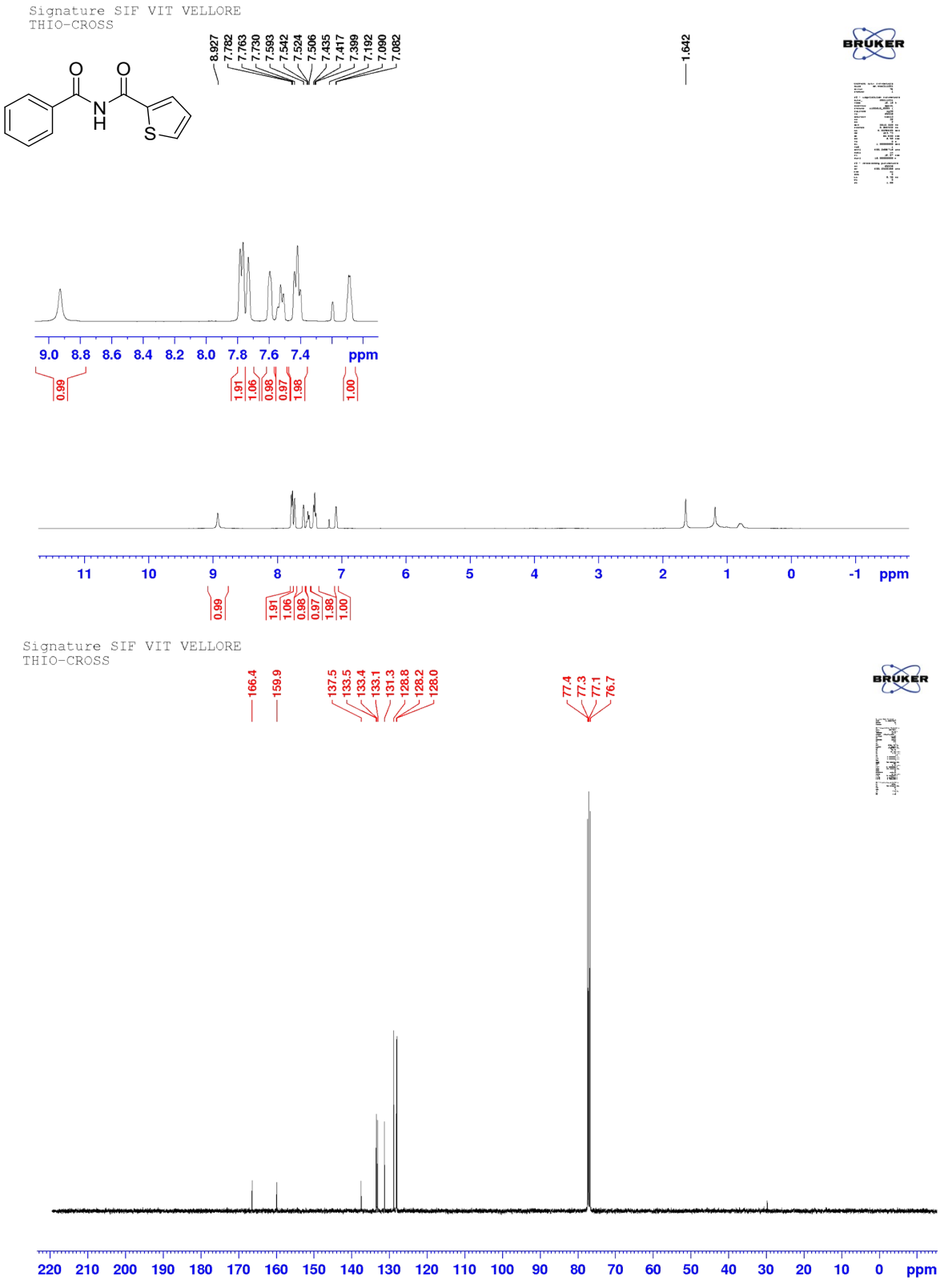
Supplementary Figure 41. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-2-methylbenzamide **4g**



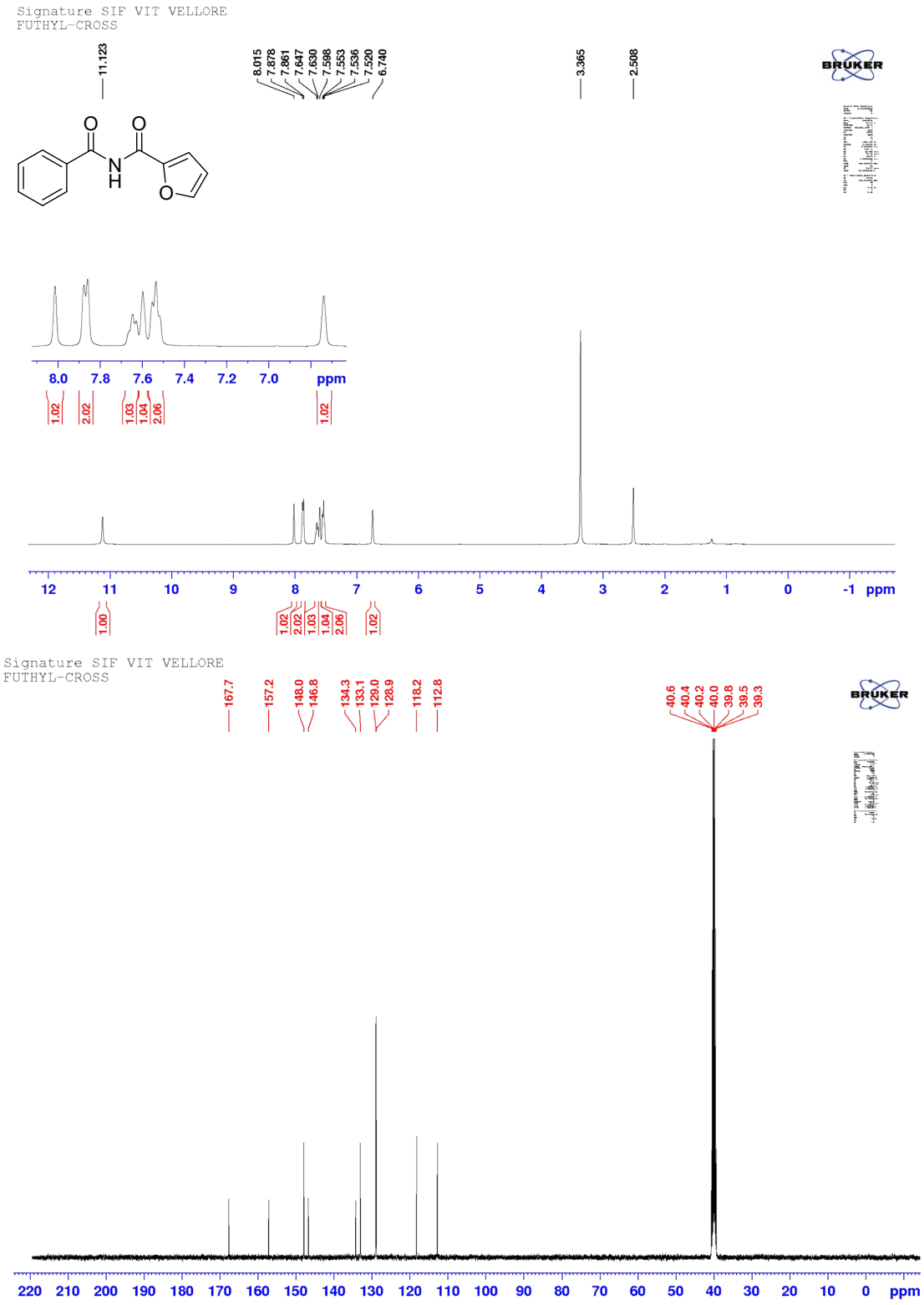
Supplementary Figure 42. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-1-naphthamide **4h**



Supplementary Figure 43. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoyl-2-naphthamide **4i**



Supplementary Figure 44. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoylthiophene-2-carboxamide **4j**



Supplementary Figure 45. ^{1}H NMR and ^{13}C NMR spectrum of *N*-benzoylfuran-2-carboxamide **4k**