NHC-Catalyzed Truce-Smiles Rearrangement of *N*-Aryl Methacrylamides Enabling the Cleavage of an Inert Aryl C-N Bond

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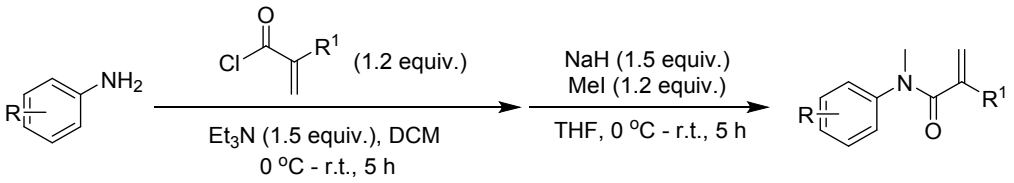
1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 AV spectrometers. ^{19}F NMR spectra were recorded on a Bruker 400 AV spectrometer. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. Coupling constant (*J*) was reported in hertz unit (Hz). The high resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS spectrometer.

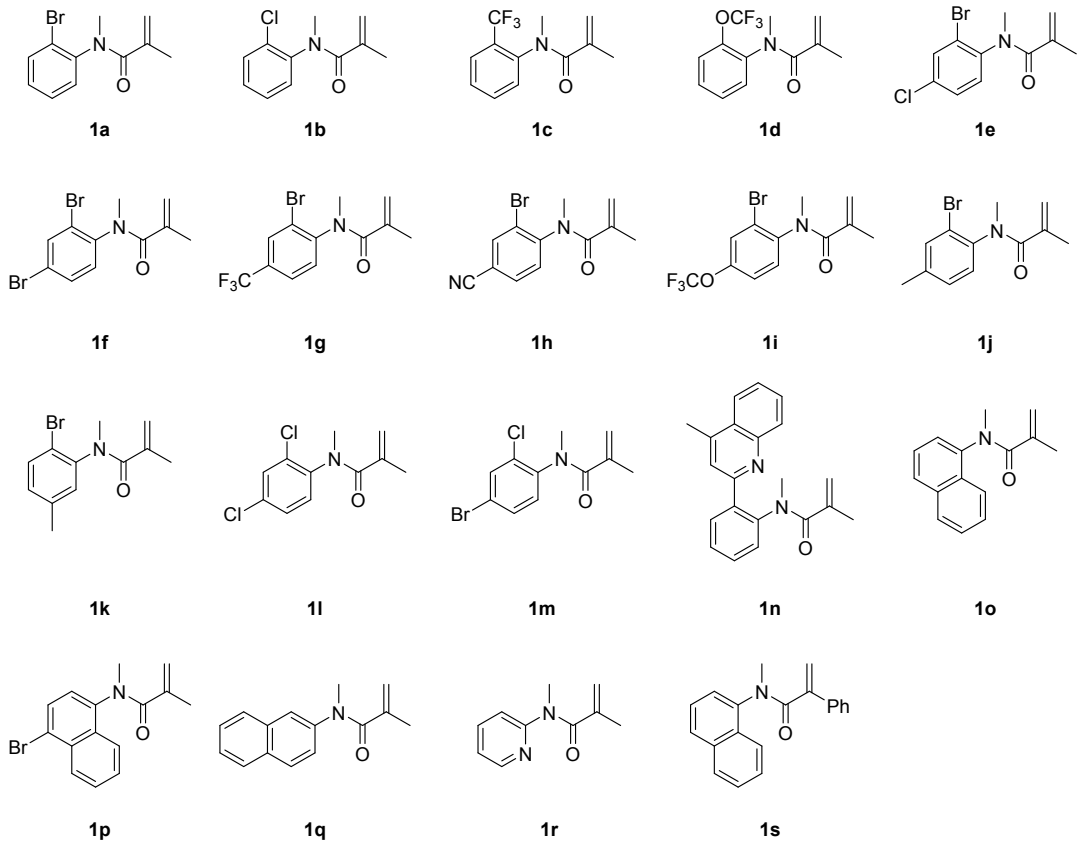
2. Preparation of *N*-Aryl Methacrylamides

The methacrylamides **1a**[1], **1b**[2], **1c**[3], **1g**[1], **1j**[4], **1k**[4], **1o**[5], **1q**[6], **1r**[7] were prepared according to the known literature[8].**1d, 1e, 1f, 1h, 1i, 1l, 1m, 1n, 1p, 1s are new compounds.**



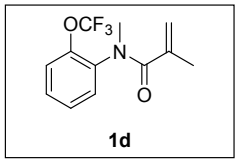
Under N_2, to a 100 mL Schleck tube with a stir bar was added amine (10 mmol), DCM (30 mL) and Et_3N (15 mmol). The reaction mixture was cooled to 0 °C, then methacryloyl chloride (12 mmol) was added. The mixture was stirred at room temperature for 5 h. The mixture was poured into brine and extracted with DCM. The combined extracts were dried over Na_2SO_4, filtered, and evaporated under vacuo. The corresponding N–H enamide was obtained after purification by flash chromatography on silica gel with PE/EA as the eluent or used without further purification.

Under N_2, to a 100 mL Schleck tube with a stir bar was added the above N–H enamide (5 mmol) and dry THF (20 mL). The reaction mixture was cooled to 0 °C, then NaH (7.5 mmol) was added. The mixture was stirred at room temperature for 30 min. Then MeI (6 mmol) were added to above solution and stirred for another 5 h. The mixture was quenched with saturated ammonium chloride solution and extracted with EtOAc. The combined extracts were dried over Na_2SO_4, filtered, and evaporated under vacuo. The corresponding Methacrylamides was obtained after purification by flash chromatography on silica gel with PE/EA as the eluent. The **1s** was obtained with 2-phenylacryloyl chloride instead of methacryloyl chloride.



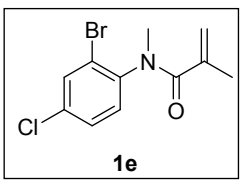
Characterization of new compounds

N-methyl-N-(2-(trifluoromethoxy)phenyl)methacrylamide (1d)



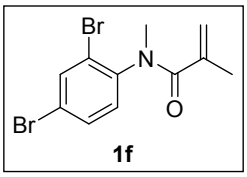
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.21 (m, 4H), 4.99 (s, 1H), 4.83 (s, 1H), 3.28 (s, 3H), 1.83 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.9, 144.5, 140.0, 136.9, 129.1, 128.5, 127.3, 120.9, 120.2 (q, J = 257.5 Hz), 118.7, 37.0, 19.7. **HRMS(ESI)** Calculated for $C_{12}H_{13}O_2NF_3^+$ ($[M+H]^+$): 260.0893, found: 260.0896.

N-(2-bromo-4-chlorophenyl)-N-methylmethacrylamide (1e)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 2.2 Hz, 1H), 7.28 (d, J = 6.9 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 4.98 (s, 2H), 3.20 (s, 3H), 1.80 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.8, 142.4, 140.0, 134.2, 133.4, 130.5, 128.8, 123.5, 119.0, 36.4, 20.2. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONBrCl^+$ ($[M+H]^+$): 287.9785, found: 287.9789.

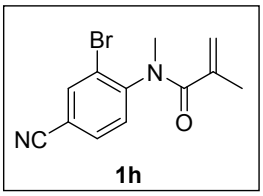
N-(2,4-dibromophenyl)-N-methylmethacrylamide (1f)



1f

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.1 Hz, 1H), 7.51-7.43 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 5.01 (d, *J* = 6.5 Hz, 2H), 3.23 (s, 3H), 1.84 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.4, 142.6, 139.7, 135.9, 131.6, 130.7, 123.5, 121.6, 118.8, 36.1, 20.0. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONBr_2^+$ ([M+H]$^+$): 331.9280, found: 331.9283.

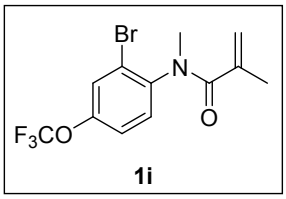
N-(2-bromo-4-cyanophenyl)-N-methylmethacrylamide (1h)



1h

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.8 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 5.06 (s, 1H), 4.97 (s, 1H), 3.24 (s, 3H), 1.85 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.3, 148.0, 139.6, 137.2, 132.2, 130.5, 123.5, 119.6, 116.5, 112.9, 36.6, 20.0. **HRMS(ESI)** Calculated for $C_{12}H_{12}ON_2Br^+$ ([M+H]$^+$): 279.0128, found: 279.0133.

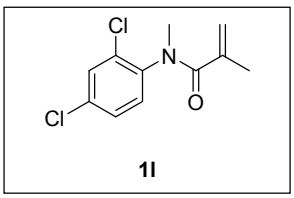
N-(2-bromo-4-(trifluoromethoxy)phenyl)-N-methylmethacrylamide (1i)



1i

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.25-7.13 (m, 2H), 4.99 (d, *J* = 10.9 Hz, 2H), 3.23 (s, 3H), 1.81 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.7, 148.2, 142.3, 139.9, 130.6, 127.7, 126.0, 123.5, 120.7, 119.0, 120.2 (q, *J* = 257.4 Hz), 36.4, 20.1. **HRMS(ESI)** Calculated for $C_{12}H_{12}O_2BrNF_3^+$ ([M+H]$^+$): 337.9998, found: 338.0001.

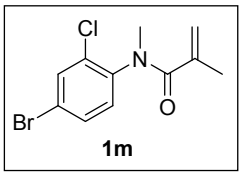
N-(2,4-dichlorophenyl)-N-methylmethacrylamide (1l)



1l

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.2 Hz, 1H), 7.25-7.20 (m, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 4.98 (s, 1H), 4.94 (s, 1H), 3.20 (s, 3H), 1.79 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.8, 140.8, 139.9, 134.0, 133.3, 130.4, 130.3, 128.1, 118.7, 36.2, 20.0. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONCl_2^+$ ([M+H]$^+$): 244.0291, found: 244.0293.

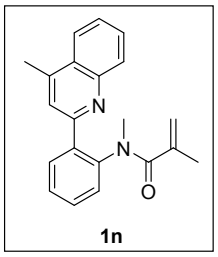
N-(4-bromo-2-chlorophenyl)-N-methylmethacrylamide (1m)



1m

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 4.99 (s, 1H), 4.95 (s, 1H), 3.21 (s, 3H), 1.80 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.8, 141.3, 139.9, 133.6, 133.2, 131.1, 130.8, 121.6, 118.9, 36.2, 20.1. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONBrCl^+$ ([M+H]$^+$): 287.9785, found: 287.9789.

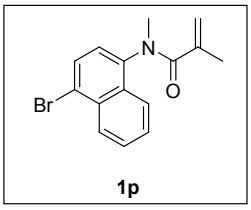
N-methyl-N-(2-(4-methylquinolin-2-yl)phenyl)methacrylamide (1n)



1n

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.61 – 7.55 (m, 1H), 7.48 – 7.40 (m, 2H), 7.36 (s, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 4.95 (s, 1H), 4.87 (s, 1H), 3.31 (s, 3H), 2.74 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.4, 156.4, 148.0, 144.8, 142.9, 140.0, 137.9, 131.3, 130.4, 129.6, 129.5, 128.6, 127.9, 126.6, 123.6, 121.9, 119.7, 38.2, 19.9, 19.0. **HRMS(ESI)** Calculated for $C_{21}H_{21}ON_2^+$ ($[M+H]^+$): 317.1648, found: 317.1652.

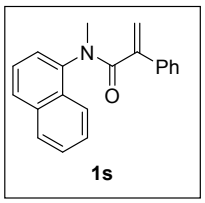
N-(4-bromonaphthalen-1-yl)-N-methylmethacrylamide (1p)



1p

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 1H), 7.92-7.76 (m, 2H), 7.53 (s, 1H), 7.40 (s, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 4.85 (s, 1H), 4.77 (s, 1H), 3.38 (s, 3H), 1.68 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 172.7, 141.3, 140.2, 133.1, 131.5, 130.7, 127.5, 127.4, 126.9, 126.2, 123.6, 122.6, 118.1, 37.7, 20.3. **HRMS(ESI)** Calculated for $C_{15}H_{15}ONBr^+$ ($[M+H]^+$): 304.0332, found: 304.0335.

N-methyl-N-(naphthalen-1-yl)-2-phenylacrylamide (1s)



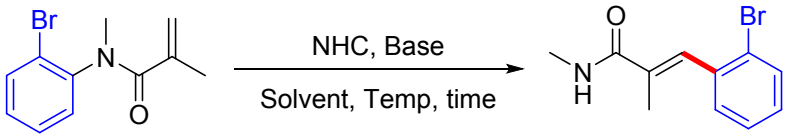
1s

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82-7.74 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.50-7.44 (m, 2H), 7.23-7.17 (m, 1H), 7.15-7.03 (m, 5H), 7.00 – 6.94 (m, 1H), 5.28 (s, 1H), 5.16 (s, 1H), 3.49 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.5, 145.7, 139.7, 136.9, 134.3, 129.8, 128.5, 128.3, 128.1, 127.7, 126.8, 126.3, 126.2, 126.0, 125.2, 122.9, 122.8, 116.7, 116.5, 116.3, 37.3, 37.3. **HRMS(ESI)** Calculated for $C_{20}H_{18}ON^+$ ($[M+H]^+$): 288.1383, found: 288.1386.

3. NHC-Catalyzed Truce-Smiles Rearrangement of *N*-Aryl Methacrylamides

3.1 Optimization of reaction conditions

Survey of the reaction parameters[a]

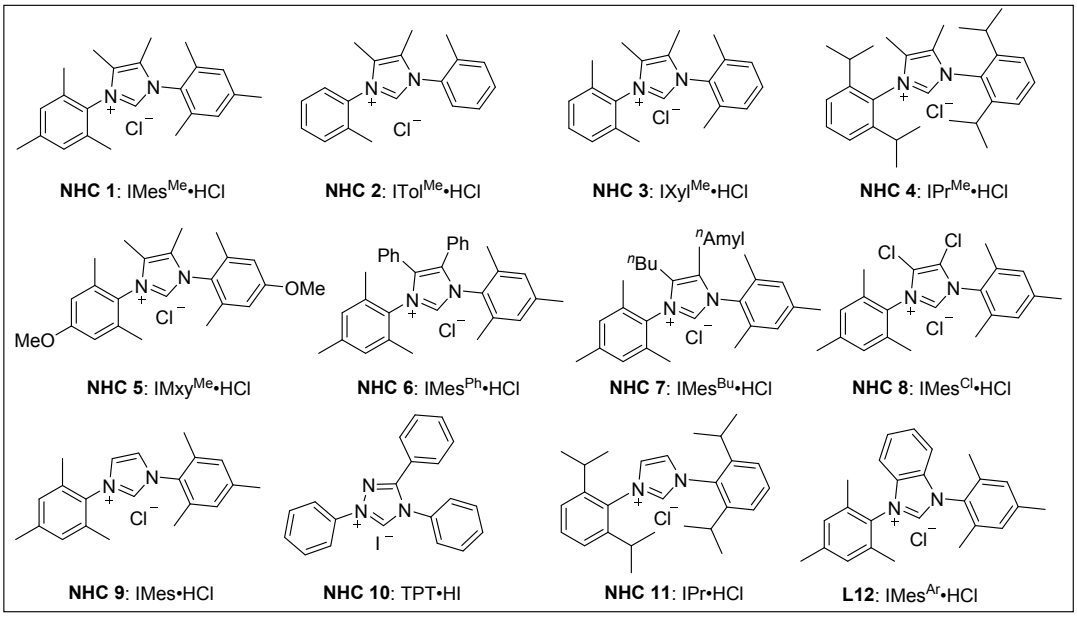


1a **2a**

Entry	NHC/mol%	Base/equiv.	Temp/ °C	Solvent/ml	Yield/%
1	**NHC 1** (20)	NaOEt (0.3)	150	Toluene (0.5)	74
2	**NHC 2** (20)	NaOEt (0.3)	150	Toluene (0.5)	Trace
3	**NHC 3** (20)	NaOEt (0.3)	150	Toluene (0.5)	35
4	**NHC 4** (20)	NaOEt (0.3)	150	Toluene (0.5)	0
5	**NHC 5** (20)	NaOEt (0.3)	150	Toluene (0.5)	68
6	**NHC 6** (20)	NaOEt (0.3)	150	Toluene (0.5)	0
7	**NHC 7** (20)	NaOEt (0.3)	150	Toluene (0.5)	36
8	**NHC 8** (20)	NaOEt (0.3)	150	Toluene (0.5)	Trace
9	**NHC 9** (20)	NaOEt (0.3)	150	Toluene (0.5)	0
10	**NHC 10** (20)	NaOEt (0.3)	150	Toluene (0.5)	0
11	**NHC 11** (20)	NaOEt (0.3)	150	Toluene (0.5)	0
12	**NHC 12** (20)	NaOEt (0.3)	150	Toluene (0.5)	0

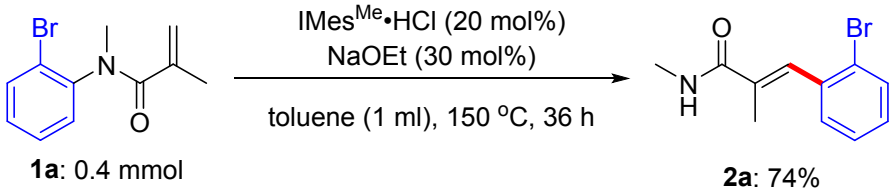
13	-[c]	NaOEt (0.3)	150	Toluene (0.5)	0
14	**NHC 1** (20)	NaO*t*-Bu (0.3)	150	Toluene (0.5)	47
16	**NHC 1** (20)	Na_2CO_3 (0.3)	150	Toluene (0.5)	34
17	**NHC 1** (20)	NaOMe (0.3)	150	Toluene (0.5)	54
18	**NHC 1** (20)	NaH (0.3)	150	Toluene (0.5)	48
19	**NHC 1** (20)	K_3PO_4 (0.3)	150	Toluene (0.5)	53
20	**NHC 1** (20)	Et_3N (0.3)	150	Toluene (0.5)	0
21	**NHC 1** (20)	DBU (0.3)	150	Toluene (0.5)	0
22	**NHC 1** (20)	DABCO (0.3)	150	Toluene (0.5)	0
23	**NHC 1** (20)	--[b]	150	Toluene (0.5)	0
24	**NHC 1** (20)	NaOEt (0.5)	150	Toluene (0.5)	51
26	**NHC 1** (20)	NaOEt (0.3)	120	Toluene (0.5)	31
27	**NHC 1** (20)	NaOEt (0.3)	150	THF (0.5)	53
28	**NHC 1** (20)	NaOEt (0.3)	150	Dioxane (0.5)	38
29	**NHC 1** (20)	NaOEt (0.3)	150	CH_3CN (0.5)	25
30	**NHC 1** (20)	NaOEt (0.3)	150	DMF (0.5)	Trace
31	**NHC 1** (20)	NaOEt (0.3)	150	Xylene (0.5	48
32	**NHC 1** (20)	NaOEt (0.3)	150	DMSO (0.5)	0
33	**NHC 1** (20)	NaOEt (0.3)	150	Toluene	56

				(1.0)	
34	**NHC 1** (10)	NaOEt (0.15)	150	Toluene (0.5)	59
35	**NHC 1** (20)	NaOEt (0.3)	150	Toluene (0.5)	62[d]



[a]Reaction conditions unless otherwise noted: **1a** (0.2 mmol), NHC (0.04 mmol), Base (0.06 mmol), Solvent (0.5 mL), 150 ^{o}C, 36 h under N_2 atmosphere. [b]No Base. [c]No NHC. [d]for 24 h.

3.2 Typical procedure and characterization of products

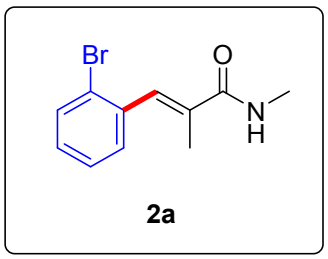


1a: 0.4 mmol

2a: 74%

To a 25 ml flame-dried Schlenk tube containing a stirring bar was added IMes^{Me}·HCl (**NHC 1**, 20 mol%, 0.08 mmol, 29.4 mg), NaOEt (0.12 mmol, 8.2 mg), toluene (1 mL) and N-(2-bromophenyl)-N-methylmethacrylamide **1a** (0.4 mmol, 101.2 mg) sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the product **2a** in 74% yield.

(*E*)-3-(2-bromophenyl)-*N*,2-dimethylacrylamide (2a)

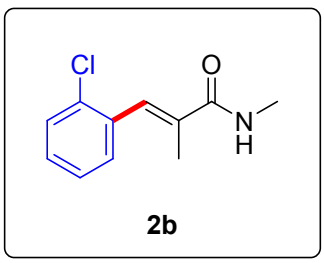


2a

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow oil (81 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J_1 = 8.0, J_2 = 1.0 Hz, 1H), 7.33-7.29 (m, 1H), 7.28-7.23 (m, 2H), 7.20-7.14 (m, 1H), 5.99 (s, 1H), 2.95 (d, J = 4.9 Hz, 3H), 1.97 (d, J = 1.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.8, 136.4, 134.0, 132.7, 132.5, 130.4, 129.2, 127.0, 124.1, 26.7, 14.2. **HRMS(ESI)** Calculated for $C_{11}H_{13}ONBr^+$ ([M+H]$^+$): 254.0175, found: 254.0179.

(*E*)-3-(2-chlorophenyl)-*N*,2-dimethylacrylamide (2b)



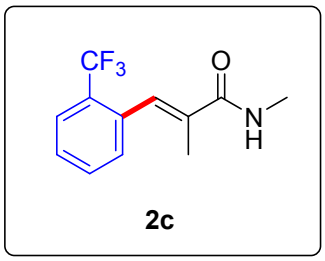
2b

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow oil (50 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.39 (m, 1H), 7.32 (s, 1H), 7.28-7.26 (m, 3H), 6.01 (s, 1H), 2.96 (d, J = 4.8 Hz, 3H), 1.99 (d, J = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.8, 134.6, 134.4, 134.0, 130.4, 130.4, 129.5,

129.0, 126.4, 26.7, 14.3. **HRMS(ESI)** Calculated for $C_{11}H_{13}ONCl^+$ ([M+H]$^+$): 210.0680, found: 210.0682.

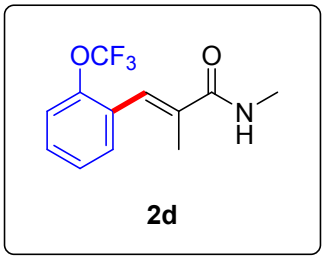
(E)-N,2-dimethyl-3-(2-(trifluoromethyl)phenyl)acrylamide (2c)



2c

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow oil (55 mg, 56% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43-7.37 (m, 2H), 7.28 (s, 1H), 6.16 (s, 1H), 2.93 (d, *J* = 4.8 Hz, 3H), 1.88 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.5, 135.0 (q, *J* = 1.8 Hz), 134.9, 131.5, 130.5, 130.0, 128.5 (q, *J* = 30.0 Hz), 127.6, 125.8 (q, *J* = 5.3 Hz), 124.0 (q, *J* = 273.7 Hz), 26.6, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -60.8. **HRMS(ESI)** Calculated for $C_{12}H_{13}ONF_3^+$ ([M+H]$^+$): 244.0943, found: 244.0949.

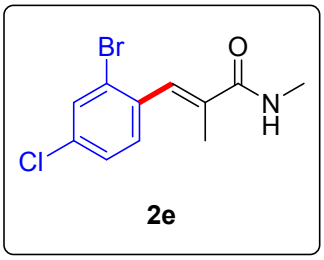
(E)-N,2-dimethyl-3-(2-(trifluoromethoxy)phenyl)acrylamide (2d)



2d

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow oil (61 mg, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34-7.23 (m, 5H), 6.35 (s, 1H), 2.91 (d, *J* = 4.8 Hz, 3H), 1.96 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.6, 146.9, 134.9, 130.7, 129.6, 129.1, 127.4, 126.4, 121.4, 120.4 (q, *J* = 256.3 Hz), 26.6, 14.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -56.7. **HRMS(ESI)** Calculated for $C_{12}H_{13}O_2NF_3^+$ ([M+H]$^+$): 260.0893, found: 269.0897.

(E)-3-(2-bromo-4-chlorophenyl)-N,2-dimethylacrylamide (2e)



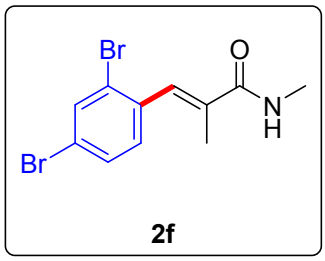
2e

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow solid (76 mg, 66% yield). mp: 62-64 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.0 Hz, 1H), 7.31-7.28 (m, 1H), 7.20 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.20 (s, 1H), 2.94 (d, *J* = 4.8 Hz, 3H), 1.95 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.4, 134.9, 134.5, 134.1, 132.3, 131.6, 131.0,

127.3, 124.4, 26.7, 14.2. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONBrCl^+$ ([M+H]$^+$): 287.9785, found: 287.9792.

(E)-3-(2,4-dibromophenyl)-N,2-dimethylacrylamide (2f)

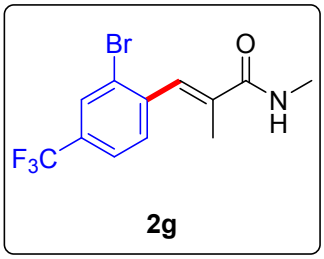


2f

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow solid (76 mg, 57% yield). mp: 73-75 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 1.9 Hz, 1H), 7.43 (dd, J_1 = 8.2 Hz, J_2 = 1.9 Hz, 1H), 7.19 (s, 1H), 7.10 (d, J = 8.2 Hz, 1H), 6.43 (d, J = 2.9 Hz, 1H), 2.93 (d, J = 4.8 Hz, 3H), 1.94 (d, J = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.3, 135.3, 134.8, 134.2, 131.6, 131.2, 130.1, 124.6, 121.8, 26.6, 14.1. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONBr_2^+$ ([M+H]$^+$): 331.9280, found: 331.9286.

(E)-3-(2-bromo-4-(trifluoromethyl)phenyl)-N,2-dimethylacrylamide (2g)

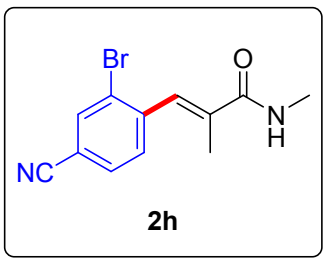


2g

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow solid (68 mg, 57% yield). mp: 102-104 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.28 (s, 1H), 6.36 (s, 1H), 2.96 (d, J = 4.8 Hz, 3H), 1.97 (d, J = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.1, 140.3, 135.3, 131.5, 131.1 (q, J = 32.5), 130.6, 129.6 (q, J = 3.8 Hz), 124.2, 122.9 (q, J = 271.3 Hz), 123.9 (q, J = 3.6 Hz), 26.7, 14.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.7. **HRMS(ESI)** Calculated for $C_{12}H_{12}ONBrF_3^+$ ([M+H]$^+$): 322.0054, found: 322.0057.

(E)-3-(2-bromo-4-cyanophenyl)-N,2-dimethylacrylamide (2h)

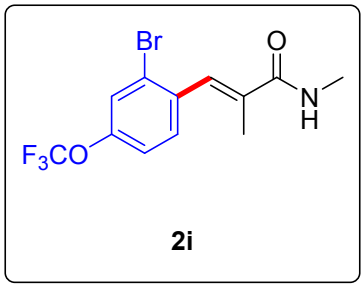


2h

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 2:1 to 1:2) as white solid (68 mg, 57% yield). mp: 132-134 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 1.5 Hz, 1H), 7.62 (dd, J_1 = 8.0, J_2 = 1.4 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.27 (s, 1H), 6.16 (s, 1H), 2.96 (d, J = 4.9 Hz,

3H), 1.97 (d, J = 1.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 168.8, 141.7, 136.0, 135.9, 131.3, 130.9, 130.6, 124.6, 117.1, 112.9, 26.8, 14.4. **HRMS(ESI)** Calculated for $C_{12}H_{10}ON_2Br^-$ ([M-H]$^-$): 276.9982, found: 276.9978.



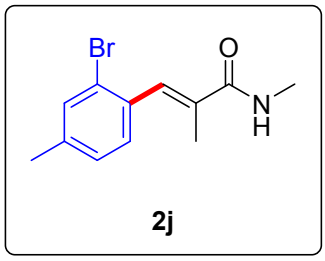
2i

(E)-3-(2-bromo-4-(trifluoromethoxy)phenyl)-N,2-dimethylacrylamide (2i)

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as white solid (76 mg, 56% yield). mp: 75-77 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 1.5 Hz, 1H), 7.29-7.24 (m, 2H), 7.19 (dd, J_1 = 8.5, J_2 = 1.1 Hz, 1H), 6.36 (d, J = 3.2 Hz, 1H), 2.95 (d, J = 4.8 Hz, 3H), 1.97 (d, J = 1.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.3, 148.4 (q, J = 1.7 Hz), 135.2, 134.6, 131.4, 131.1, 125.1, 124.3, 120.2 (q, J = 258.5 Hz), 119.4, 26.7, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -58.0. **HRMS(ESI)** Calculated for $C_{12}H_{10}O_2NBrF_3^-$ ([M-H]$^-$): 335.9847, found: 335.9858.

(E)-3-(2-bromo-4-methylphenyl)-N,2-dimethylacrylamide (2j)

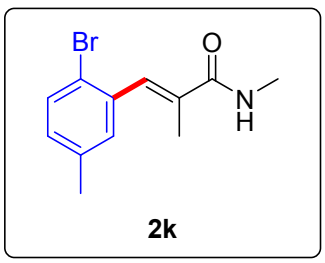


2j

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow oil (59 mg, 55% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.24 (s, 1H), 7.16-7.05 (m, 2H), 6.29 (s, 1H), 2.93 (d, J = 4.8 Hz, 3H), 2.33 (s, 3H), 1.96 (d, J = 1.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.9, 139.4, 133.4, 133.3, 133.0, 132.5, 130.1, 127.7, 123.9, 26.6, 20.7, 14.1. **HRMS(ESI)** Calculated for $C_{12}H_{15}ONBr^+$ ([M+H]$^+$): 268.0032, found: 268.0037.

(E)-3-(2-bromo-5-methylphenyl)-N,2-dimethylacrylamide (2k)



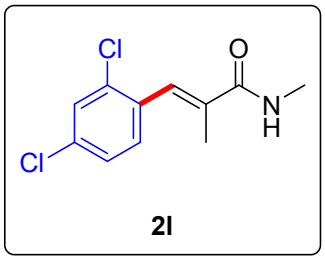
2k

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as white solid (61 mg, 57% yield). mp: 120-122 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 1H), 7.24 (s, 1H), 7.03 (d, J = 0.9 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.39 (s, 1H), 2.93 (d, J = 4.8 Hz, 3H), 2.29

(s, 3H), 1.96 (d, J = 1.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.7, 136.7, 136.0, 133.5, 132.7, 132.2, 130.9, 129.9, 120.5, 26.6, 20.8, 14.1. **HRMS(ESI)** Calculated for $C_{12}H_{15}ONBr^+$ ($[M+H]^+$): 268.0032, found: 268.0032.

(E)-3-(2,4-dichlorophenyl)-N,2-dimethylacrylamide (2l)

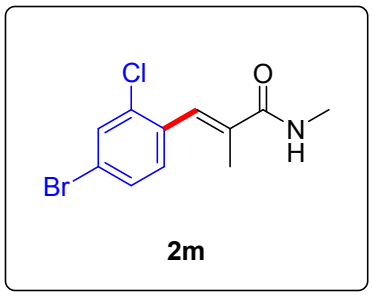


2l

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as white solid (42 mg, 43% yield). mp: 76-78 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 2.0 Hz, 1H), 7.27-7.23 (m, 2H), 7.19 (d, J = 8.3 Hz, 1H), 6.23 (s, 1H), 2.94 (d, J = 4.8 Hz, 3H), 1.97 (d, J = 1.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.4, 134.7, 134.6, 134.1, 133.1, 131.1, 129.4, 129.3, 126.7, 26.7, 14.3. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONCl_2^+$ ($[M+H]^+$): 244.0291, found: 244.0297.

(E)-3-(4-bromo-2-chlorophenyl)-N,2-dimethylacrylamide (2m)

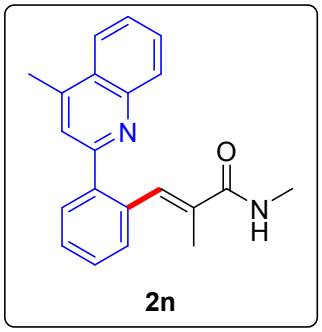


2m

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow solid (74 mg, 64% yield). mp: 79-81 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 1.9 Hz, 1H), 7.39 (dd, J_1 = 8.3, J_2 = 1.9 Hz, 1H), 7.24 (s, 1H), 7.12 (d, J = 8.3 Hz, 1H), 6.26 (s, 1H), 2.94 (d, J = 4.8 Hz, 3H), 1.96 (d, J = 1.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.4, 134.7, 134.6, 133.5, 132.0, 131.3, 129.6, 129.4, 121.7, 26.7, 14.2. **HRMS(ESI)** Calculated for $C_{11}H_{12}ONBrCl^+$ ($[M+H]^+$): 287.9785, found: 287.9791.

(E)-N,2-dimethyl-3-(2-(4-methylquinolin-2-yl)phenyl)acrylamide (2n)



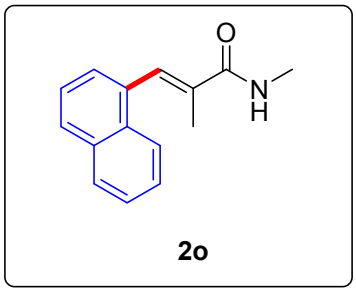
2n

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as white solid (95 mg, 75% yield). mp: 104-106 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.74-7.65 (m, 2H), 7.58-7.52 (m, 1H), 7.45-7.38 (m, 2H),

7.34 (s, 1H), 7.33-7.29 (m, 1H), 7.26 (s, 1H), 6.21 (s, 1H), 2.79 (d, J = 4.8 Hz, 3H), 2.69 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.2, 158.5, 147.6, 144.2, 140.2, 134.7, 132.7, 132.7, 129.9, 129.7, 129.6, 129.3, 128.2, 127.9, 126.8, 126.2, 123.7, 123.1, 26.4, 18.7, 14.2. **HRMS(ESI)** Calculated for $C_{21}H_{21}ON_2^+$ ([M+H]$^+$): 317.1648, found: 317.1654.

(E)-N,2-dimethyl-3-(naphthalen-1-yl)acrylamide (2o)

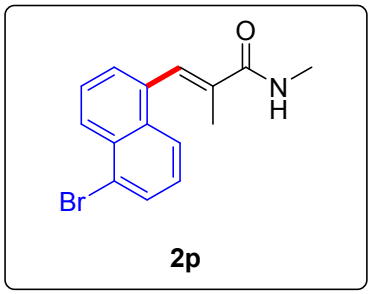


2o

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as colorless oil (76 mg, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.88 (m, 1H), 7.88-7.82 (m, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.52-7.42 (m, 3H), 7.30 (d, J = 7.0 Hz, 1H), 6.21 (s, 1H), 2.98 (d, J = 4.8 Hz, 3H), 1.95 (d, J = 1.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.7, 133.7, 133.5, 133.4, 132.5, 131.5, 128.4, 128.1, 126.4, 126.1, 126.0, 125.1, 124.8, 26.7, 14.3. **HRMS(ESI)** Calculated for $C_{15}H_{16}ON^+$ ([M+H]$^+$): 226.1226, found: 226.1231.

(E)-3-(5-bromonaphthalen-1-yl)-N,2-dimethylacrylamide (2p)

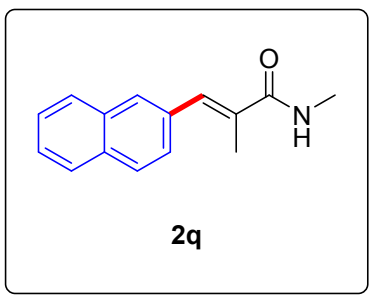


2p

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow solid (90 mg, 74% yield). mp: 93-95 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 7.87-7.76 (m, 3H), 7.57-7.51 (m, 1H), 7.35-7.24 (m, 2H), 6.28 (s, 1H), 2.98 (d, J = 4.8 Hz, 3H), 1.92 (d, J = 1.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 169.4, 134.1, 133.9, 132.7, 132.1, 131.9, 130.1, 127.2, 127.2, 126.4, 126.3, 124.7, 123.3, 26.7, 14.2. **HRMS(ESI)** Calculated for $C_{15}H_{15}ONBr^+$ ([M+H]$^+$): 304.0332, found: 304.0337.

(E)-N,2-dimethyl-3-(naphthalen-2-yl)acrylamide (2q)

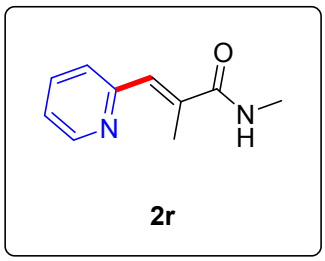


2q

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as white solid (33 mg, 36% yield). mp: 111-113 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.81 (m, 3H), 7.80 (s, 1H), 7.54-7.48 (m, 3H), 7.47-7.43 (m, 1H), 6.03 (s, 1H), 2.98 (d, *J* = 4.8 Hz, 3H), 2.19 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.3, 133.8, 133.7, 133.2, 132.7, 132.3, 128.6, 128.1, 127.9, 127.7, 127.0, 126.4, 126.4, 26.8, 14.4. **HRMS(ESI)** Calculated for $C_{15}H_{16}ON^+$ ([M+H]$^+$): 226.1226, found: 226.1231.

(E)-N,2-dimethyl-3-(pyridin-2-yl)acrylamide (2r)

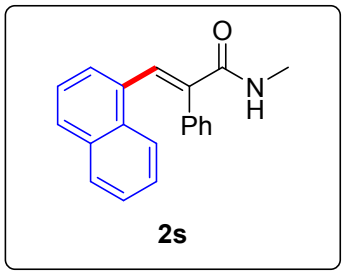


2r

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow oil (37 mg, 52% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64-8.61 (m, 1H), 7.71-7.65 (m, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 1.1 Hz, 1H), 7.20-7.14 (m, 1H), 6.49 (s, 1H), 2.93 (d, *J* = 4.8 Hz, 3H), 2.33 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 170.2, 155.3, 149.1, 136.1, 135.7, 131.6, 125.3, 122.0, 26.6, 14.2. **HRMS(ESI)** Calculated for $C_{11}H_{12}ON_2Na^+$ ([M+Na]$^+$): 199.0842, found: 199.0847.

(E)-N-methyl-3-(naphthalen-1-yl)-2-phenylacrylamide (2s)



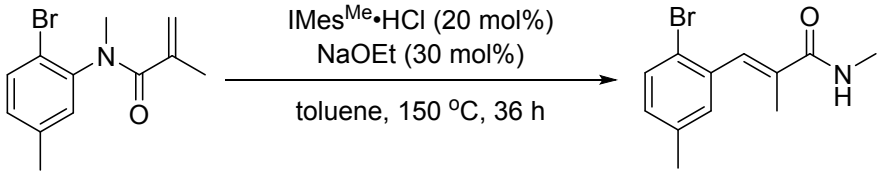
2s

Purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) as yellow solid (17 mg, 15% yield). mp: 148-150 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.56-7.42 (m, 2H), 7.26-7.23 (m, 3H), 7.16-7.12 (m, 2H), 7.11-7.07 (m, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 5.66 (s, 1H), 2.89 (d, *J* = 4.9 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 167.6, 137.1, 135.7, 135.2, 133.2, 132.6, 132.1, 130.1, 128.8, 128.4, 128.2, 128.1, 127.4, 126.2, 125.8, 124.9, 124.3, 26.8. **HRMS(ESI)** Calculated for $C_{20}H_{17}ONNa^+$ ([M+Na]$^+$): 310.1202, found: 310.1206.

3.3 Gram-scale reaction

Experimental procedure:

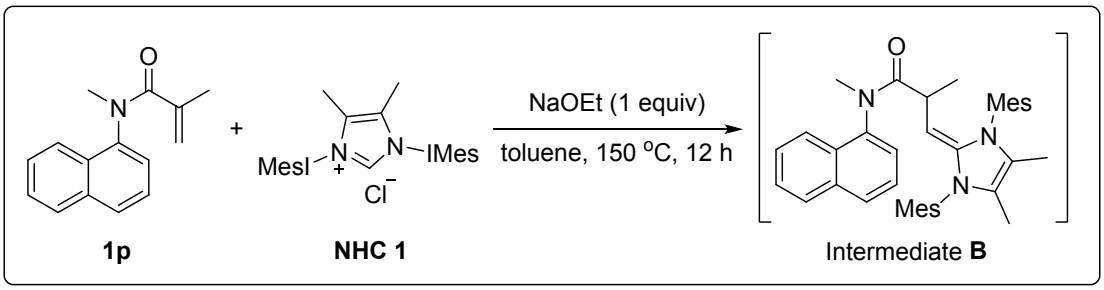


1k: 5 mmol

2k: 58% (0.78 g)

To a 250 ml flame-dried Schlenk tube containing a stirring bar was added $IMes^{Me}$·HCl (1 mmol, 370 mg), NaOEt (1.05 mmol, 71.4 mg), N-(2-bromo-5-methylphenyl)-N-methylmethacrylamide **1k** (5 mmol, 1335 mg) and toluene (12.5 mL) sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was extracted with ethyl acetate. Then, the solvent was removed under vacuum and the residue was purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1 to 1:1) to provide the product **2k** in 58% yield (0.78g, off white solid).

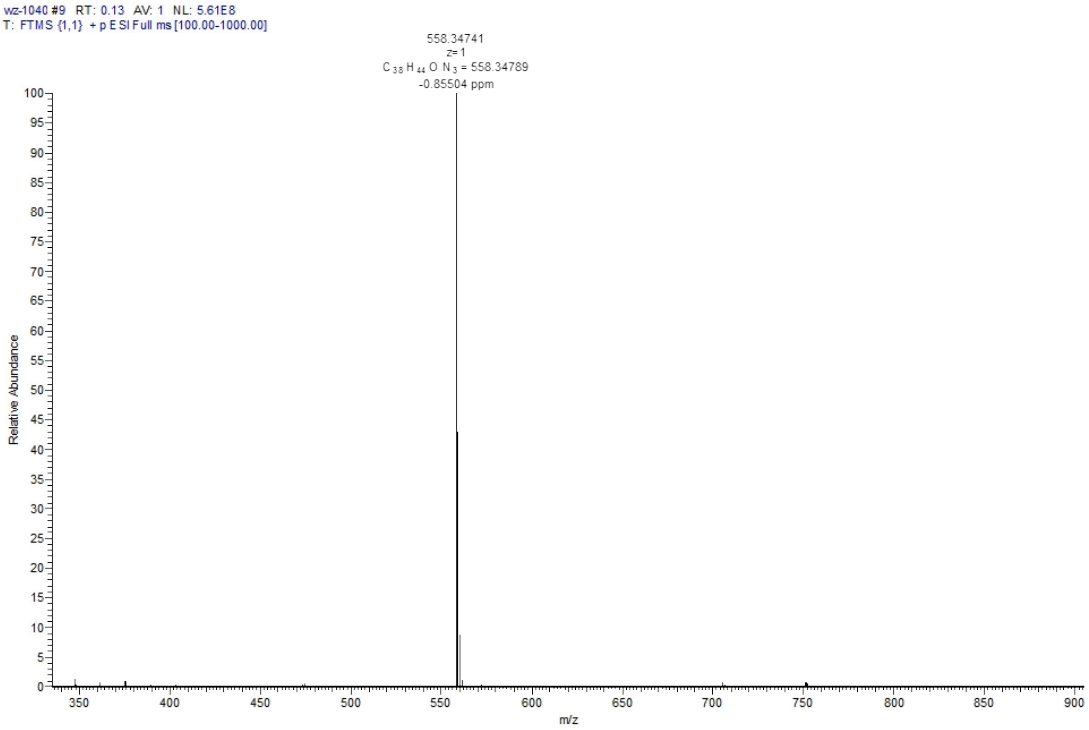
4. Mechanistic Experiments

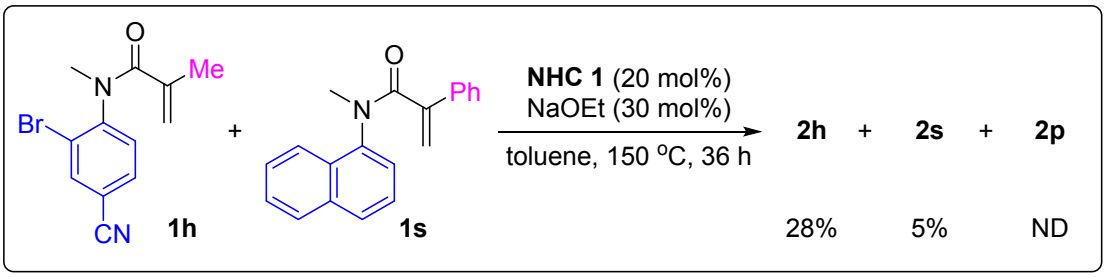


To a 25 ml flame-dried Schlenk tube containing a stirring bar was added $IMes^{Me}$·HCl (0.2 mmol, 74 mg), NaOEt (0.2 mmol, 13.6 mg), toluene (1 mL) and N-methyl-N-(naphthalen-1-yl)methacrylamide (0.2 mmol, 45 mg) sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 12 h. After completion, the reaction mixture was directly analyzed by HRMS and the possible intermediate **B** was detected which might be involved in the catalytic cycle.

HRMS(ESI) Calculated for $C_{38}H_{44}ON_3^+$ ([M+H]$^+$): 558.3479, found: 558.3474.

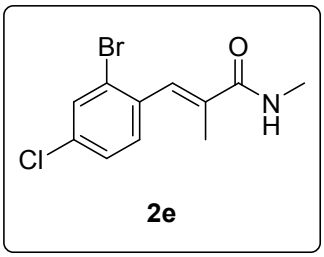
HRMS (ESI) spectra for the intermediate **B**





To a 25 ml flame-dried Schlenk tube containing a stirring bar was added **NHC 1** (0.08 mmol, 29.4 mg), NaOEt (0.12 mmol, 8.2 mg), toluene (1 mL), N-(2-bromo-4-cyanophenyl)-N-methylmethacrylamide **1h** (0.2 mmol, 55.6 mg), and N-methyl-N-(naphthalen-1-yl)-2-phenylacrylamide **1s** (0.2 mmol, 57.4 mg) sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was diluted with ethyl acetate (5.0 mL) and filtered through a short pad silica gel washing with ethyl acetate (20 mL). The filtrate was concentrated and purified by silica gel column chromatography to provide the products **2h** and **2s** in 28% and 5% yields respectively. However, the cross product **2p** failed to be detected.

5. X-Ray Crystallography Data for 2e



2e

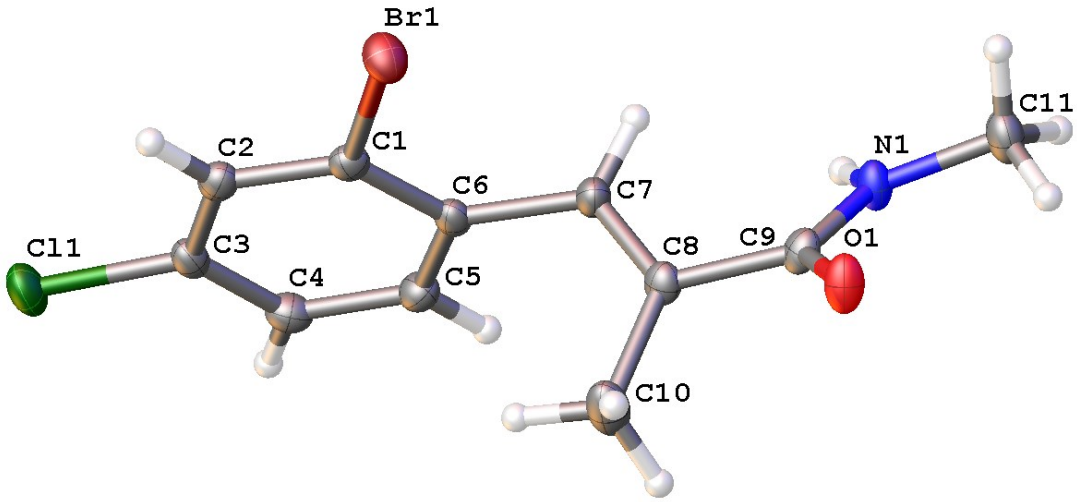


Table 1. Crystal data and structure refinement for **2e**.

Identification code	2e	
Empirical formula	C11 H11 Br Cl N O	
Formula weight	288.57	
Temperature	173.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 9.7336(5) Å	α= 90°.
	b = 9.4426(5) Å	β= 90°.
	c = 12.9051(8) Å	γ = 90°.
Volume	1186.11(11) $Å^3$	
Z	4	
Density (calculated)	1.616 Mg/m^3	
Absorption coefficient	4.460 mm^{-1}	
F(000)	576	
Crystal size	0.06 x 0.05 x 0.02 mm^3	
Theta range for data collection	5.679 to 54.844°.	

Index ranges	-10<=h<=11, -11<=k<=6, -15<=l<=15
Reflections collected	5057
Independent reflections	1866 [R(int) = 0.0383]
Completeness to theta = 53.594°	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.4809
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1866 / 1 / 138
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0697
R indices (all data)	R1 = 0.0283, wR2 = 0.0702
Absolute structure parameter	0.05(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.315 and -0.431 e.$Å^{-3}$

.

6. References

[1] Y. Ping, K. Wang, Q. Pan, Z. Ding, Z. Zhou, Y. Guo and W. Kong, *ACS Catal.* 2019, **9**, 7335.

[2] V. G. Correia, J. C. Abreu, C. A. E. Barata and L. H. Andrade, *Org. Lett.* 2017, **19**, 1060.

[3] X. Yi, S. Lei, W. Liu, F. Che, C. Yu, X. Liu, Z. Wang, X. Zhou and Y. Zhang, *Org. Lett*. 2020, **22**, 4583.

[4] X. Liu, B. Li and Z. Gu, *J. Org. Chem.* 2015, **80**, 7547.

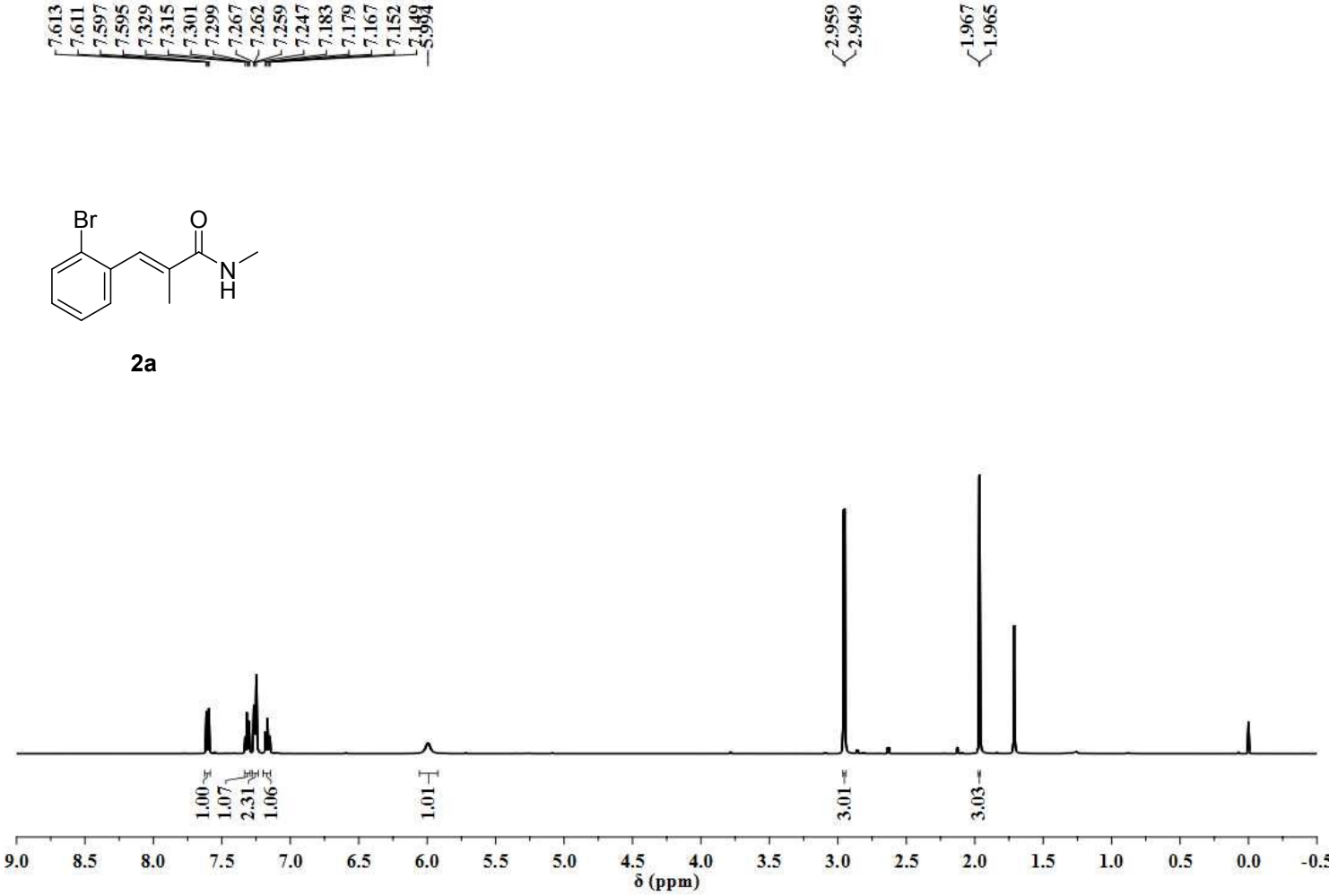
[5] J. Zhao, P. Li, Y. Xu, Y. Shi and F. Li, *Org. Lett*. 2019, **21**, 9386.

[6] M.-Z. Zhang, X. Wang, M.-Y. Gong, L. Chen, W.-B. Shi, S.-H. He, Y. Jiang and T. Chen, *Org. Biomol. Chem*. 2018, **16**, 5197.

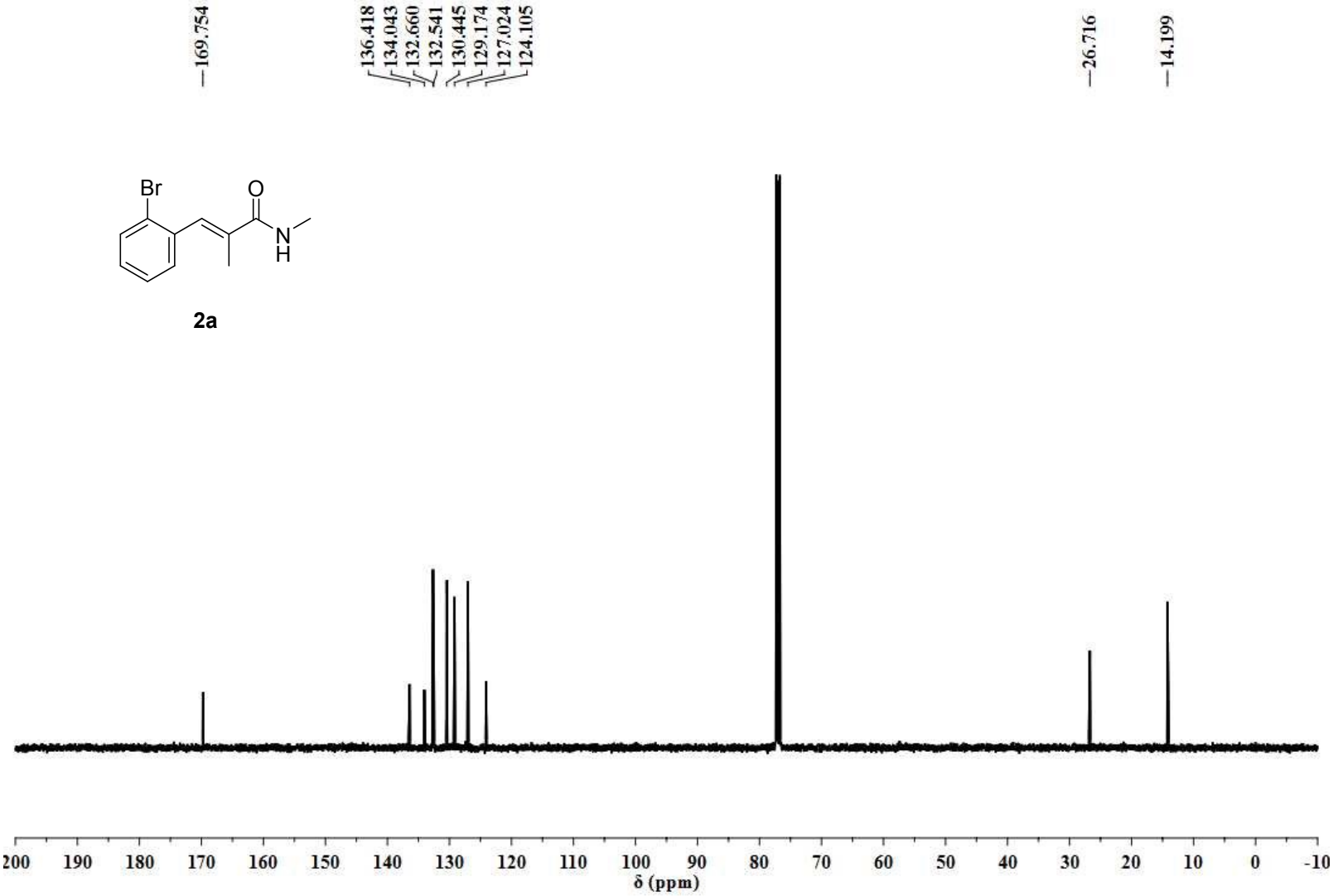
[7] W. Kong, M. Casimiro, N. Fuentes, E. Merino and C. Nevado, *Angew. Chem. Int. Ed*. 2013, **52**, 13086.

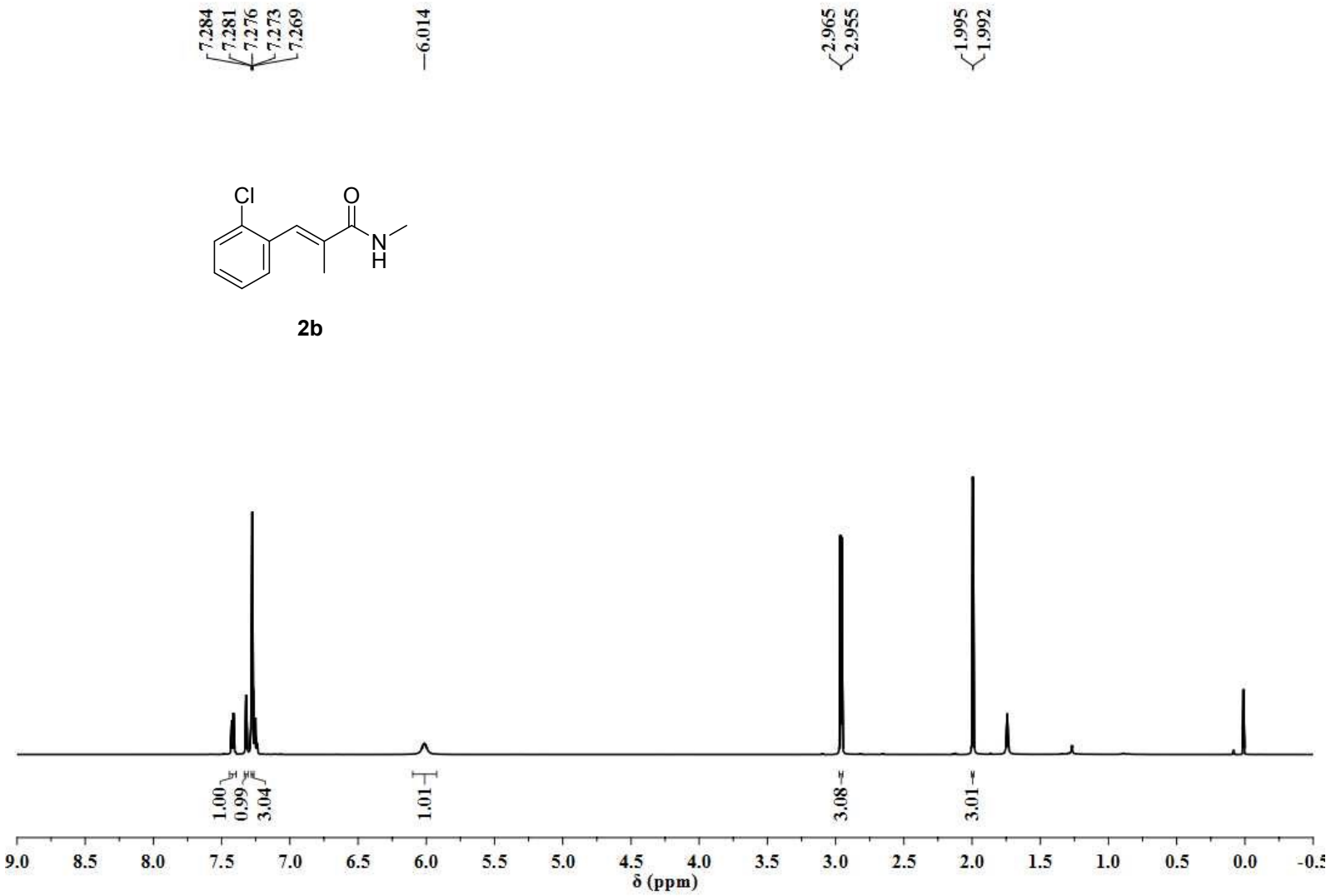
[8] (a) Y.-L. Li, J.-B. Wang, X.-L. Wang, Y. Cao and J. Deng, *Eur. J. Org. Chem.* 2017, 6052. (b) D. B. Bagal, S.-W. Park, H.-J. Song and S. Chang, *Chem. Commun.* 2017, **53**, 8798.

7. ^{1}H, ^{13}C and ^{19}F NMR Spectra

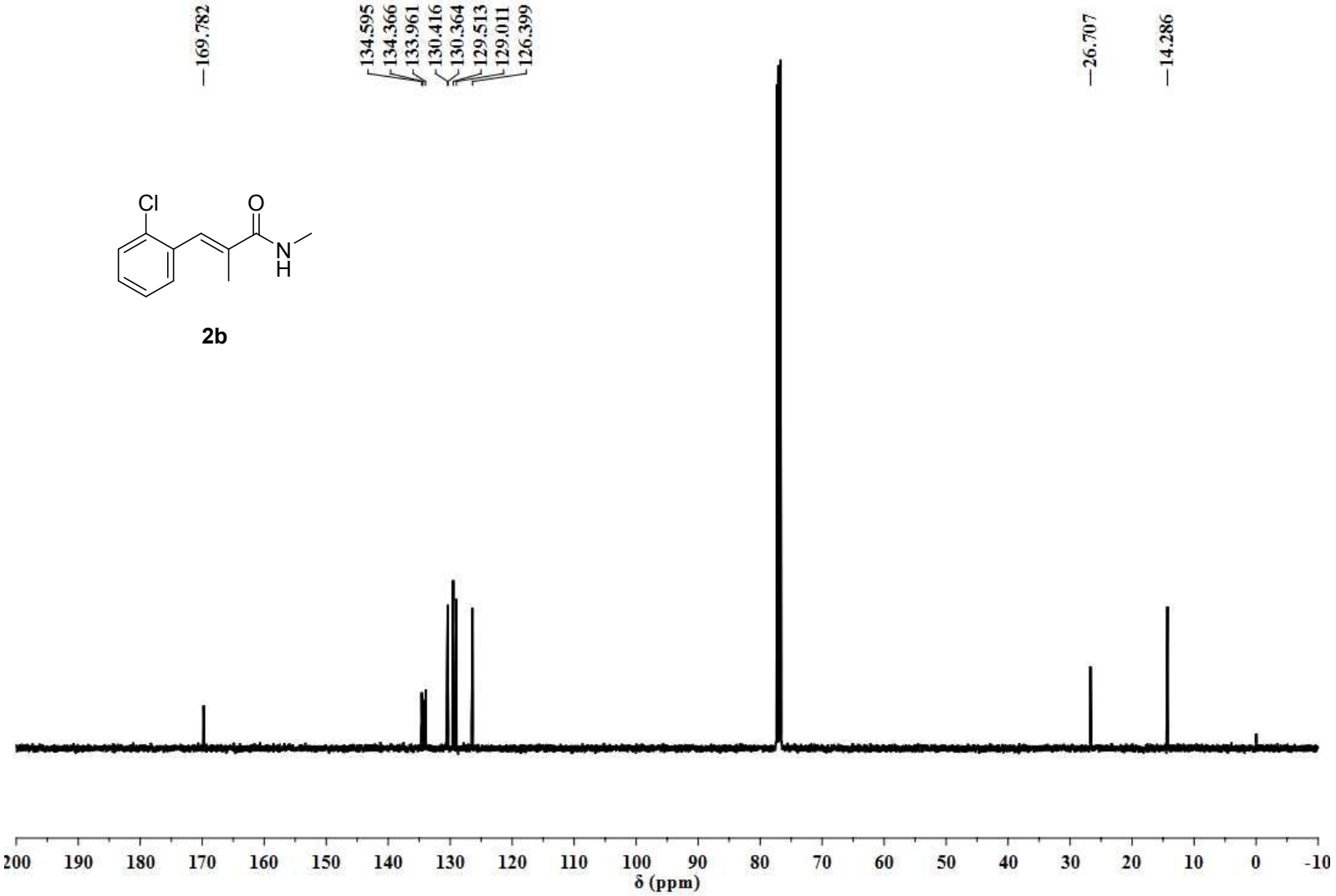


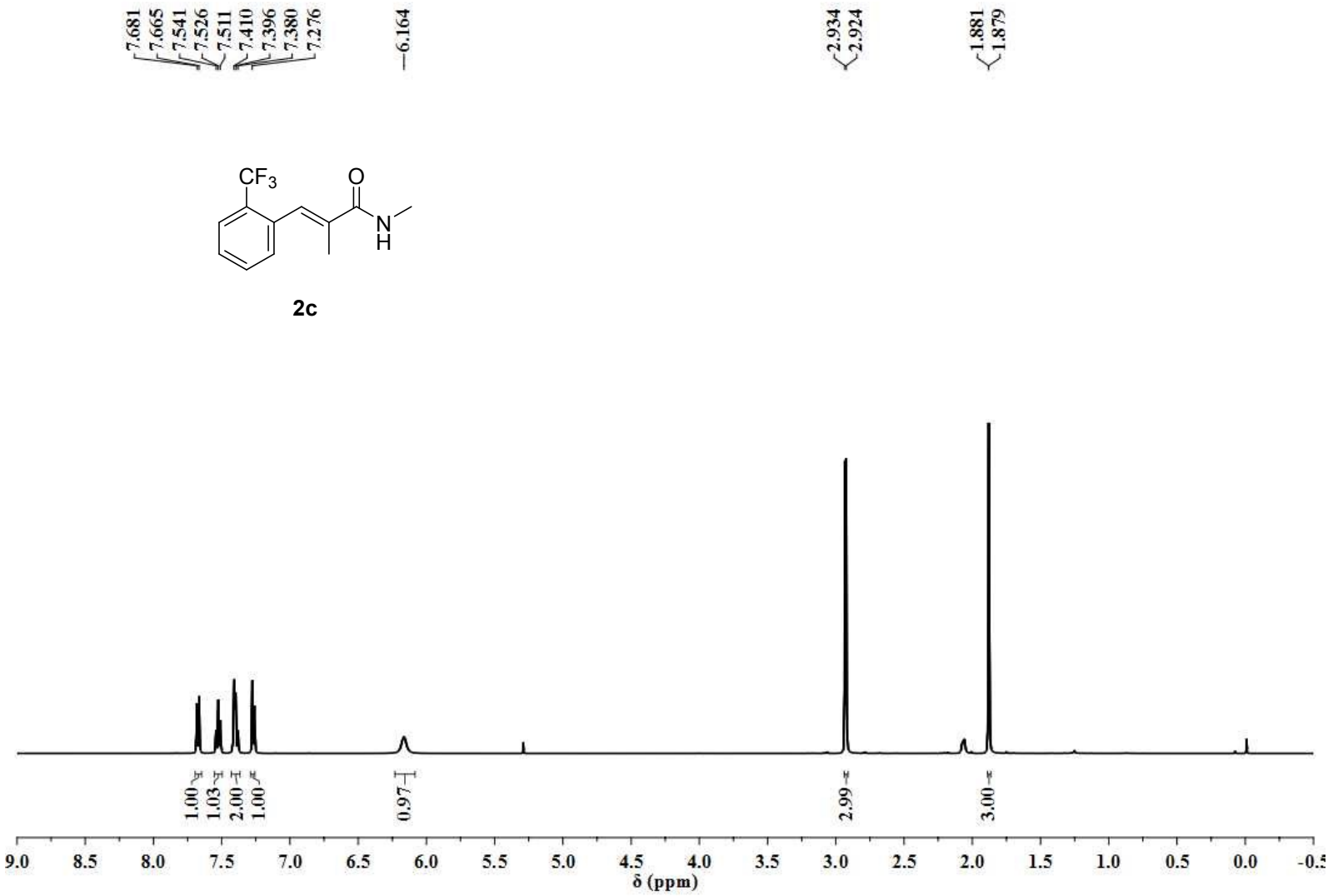
2a


169.754
136.418
134.043
132.660
132.541
130.445
129.174
127.024
124.105
26.716
14.199
Br
O
N
H
2a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

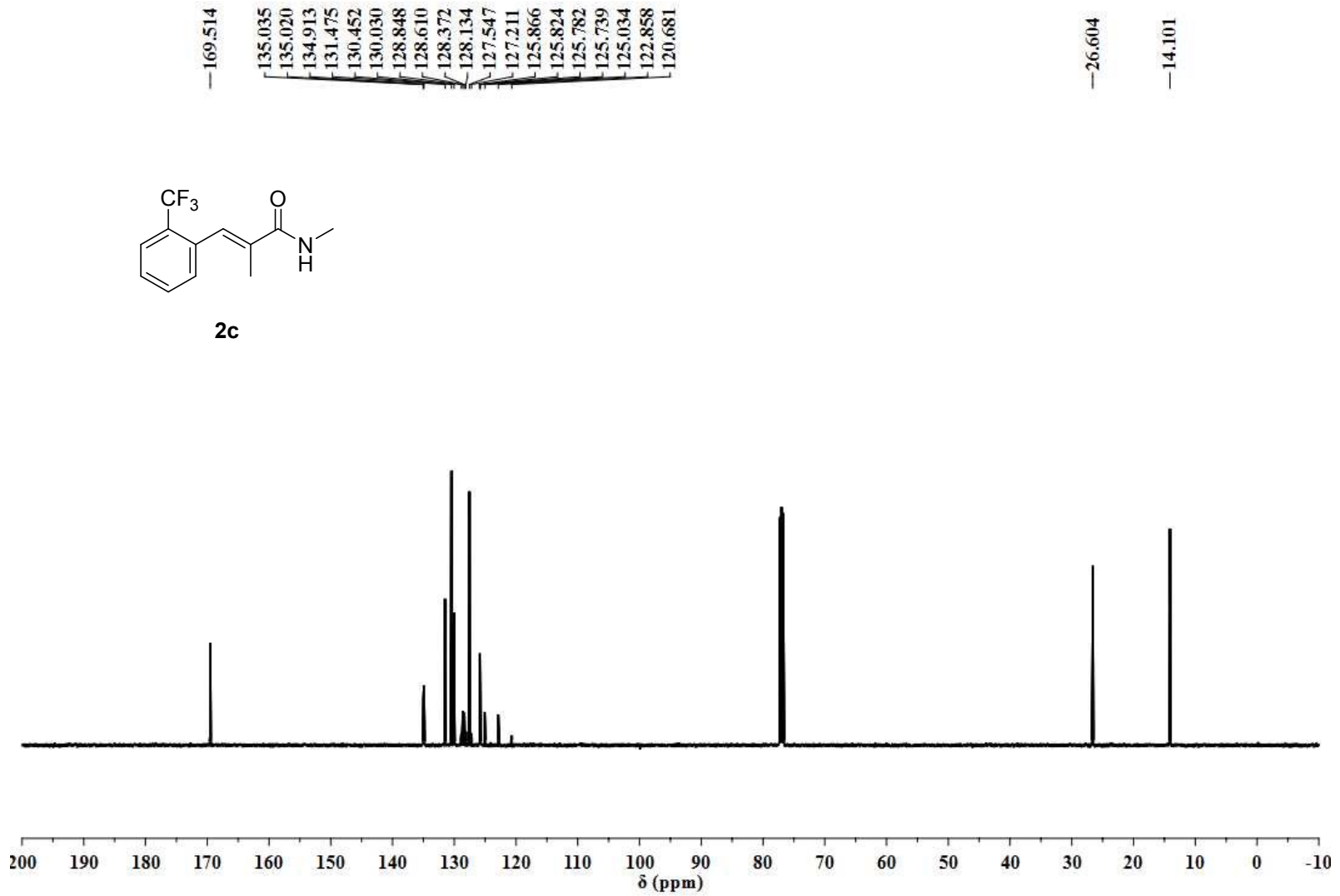

7.284
7.281
7.276
7.273
7.269
6.014
2.965
2.955
1.995
1.992
Cl
O
N
H
1.00
0.99
3.04
1.01
3.08
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

2b


169.782
134.595
134.366
133.961
130.416
130.364
129.513
129.011
126.399
26.707
14.286
Cl
O
N
H
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

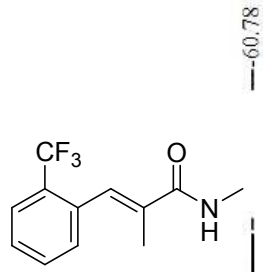

7.681
7.665
7.541
7.526
7.511
7.410
7.396
7.380
7.276
6.164
2.934
2.924
1.881
1.879
CF3
O
N
H
1.00
1.03
2.00
1.00
0.97
2.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

2c

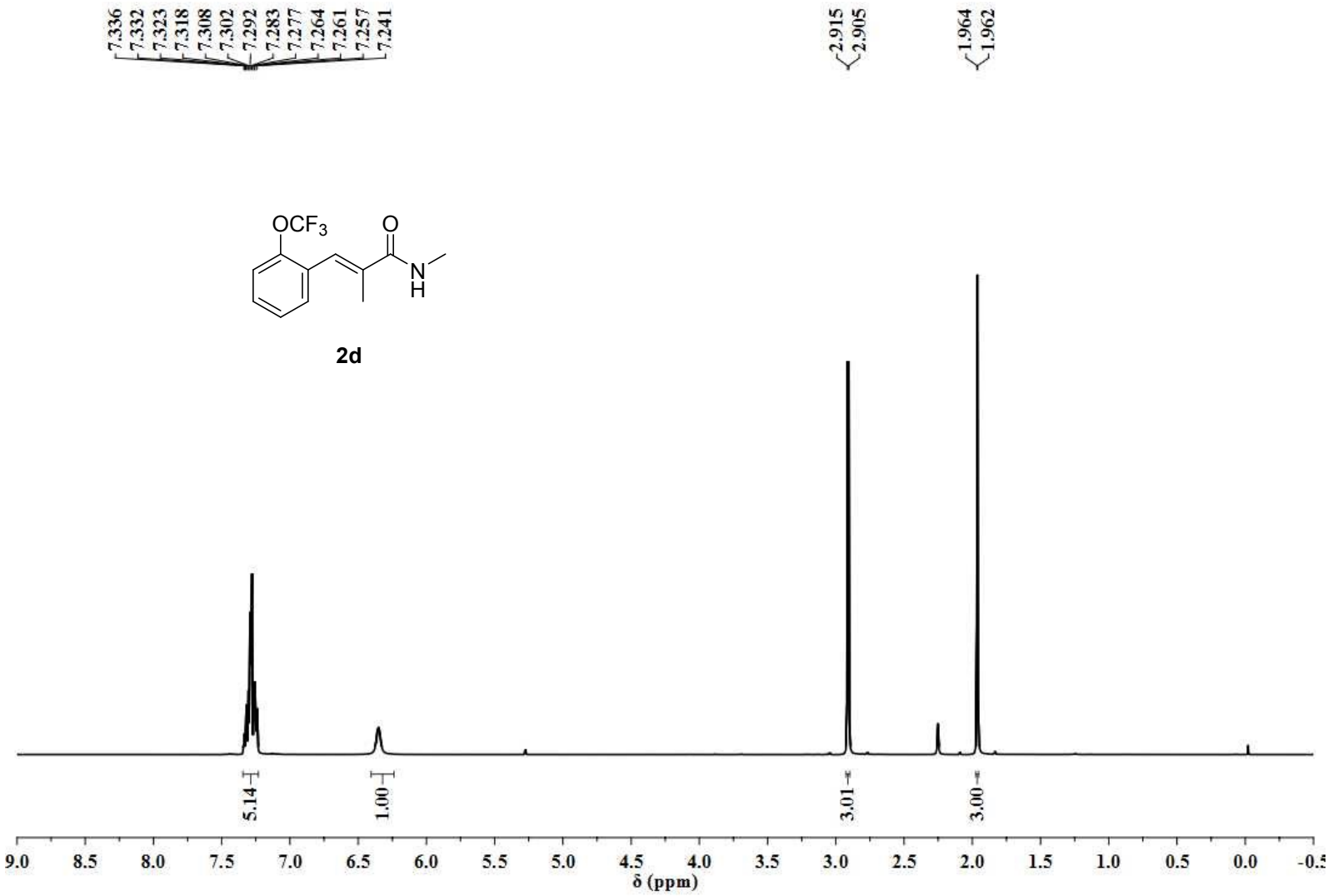

169.514
135.035
135.020
134.913
131.475
130.452
130.030
128.848
128.610
128.372
128.134
127.547
127.211
125.866
125.824
125.782
125.739
125.034
122.858
120.681
26.604
14.101
CF3
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

2c

ZBW-WZ-860-F



2c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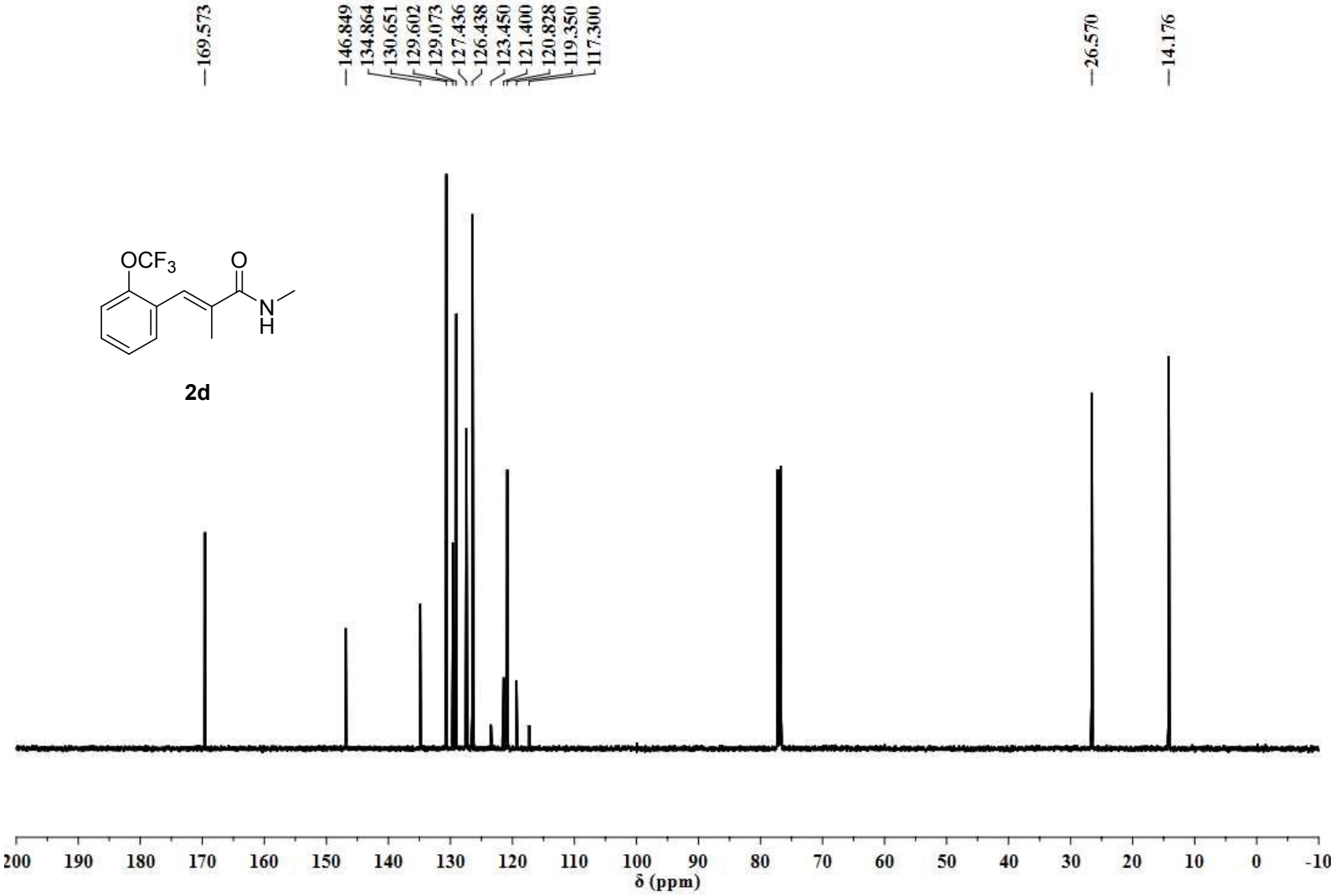
7.332
7.323
7.318
7.308
7.302
7.292
7.283
7.277
7.264
7.261
7.257
7.241
2.915
2.905
1.964
1.962
OCF3
O
N
H
2d
5.14
1.00
3.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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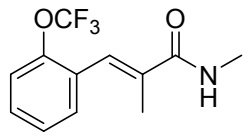
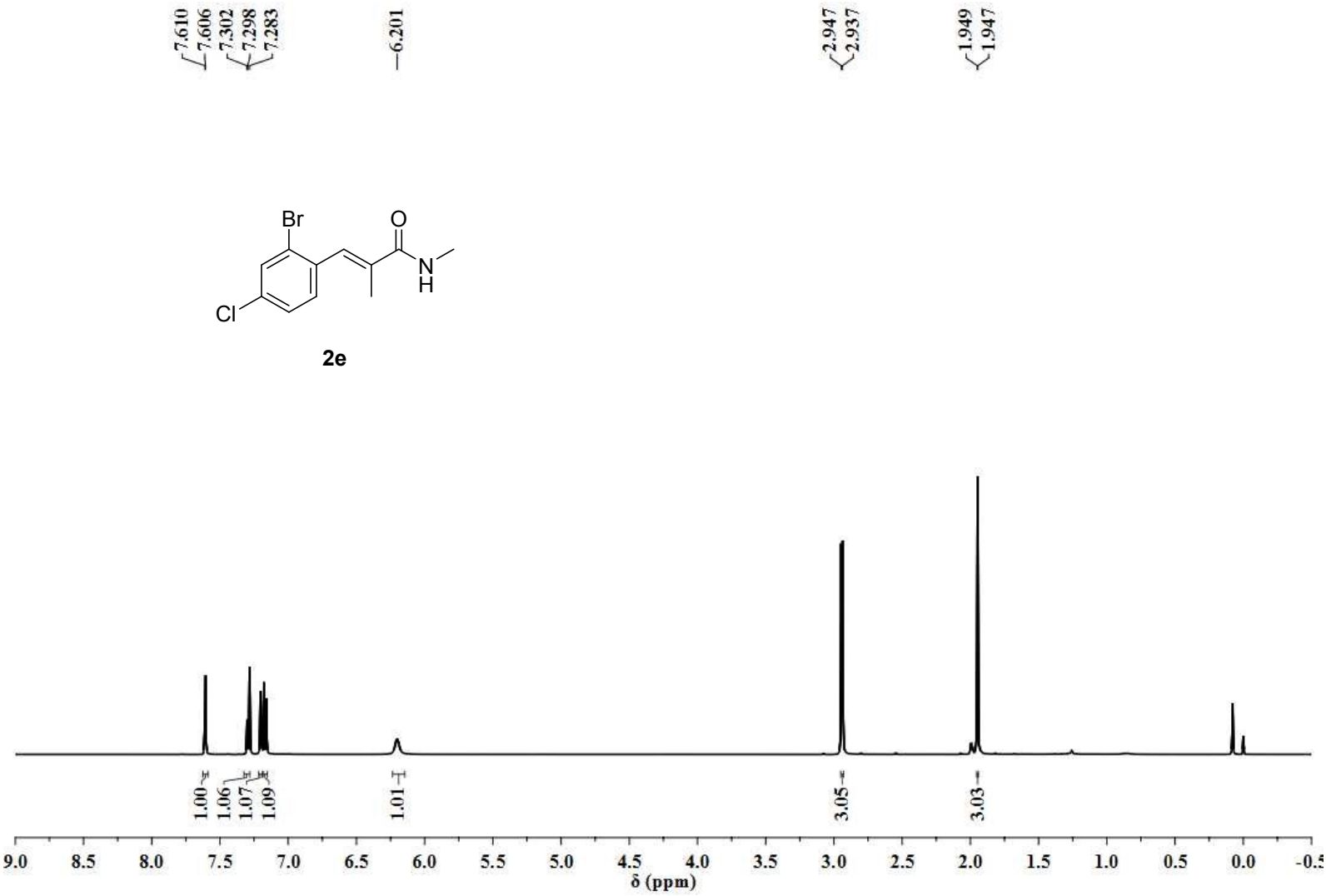
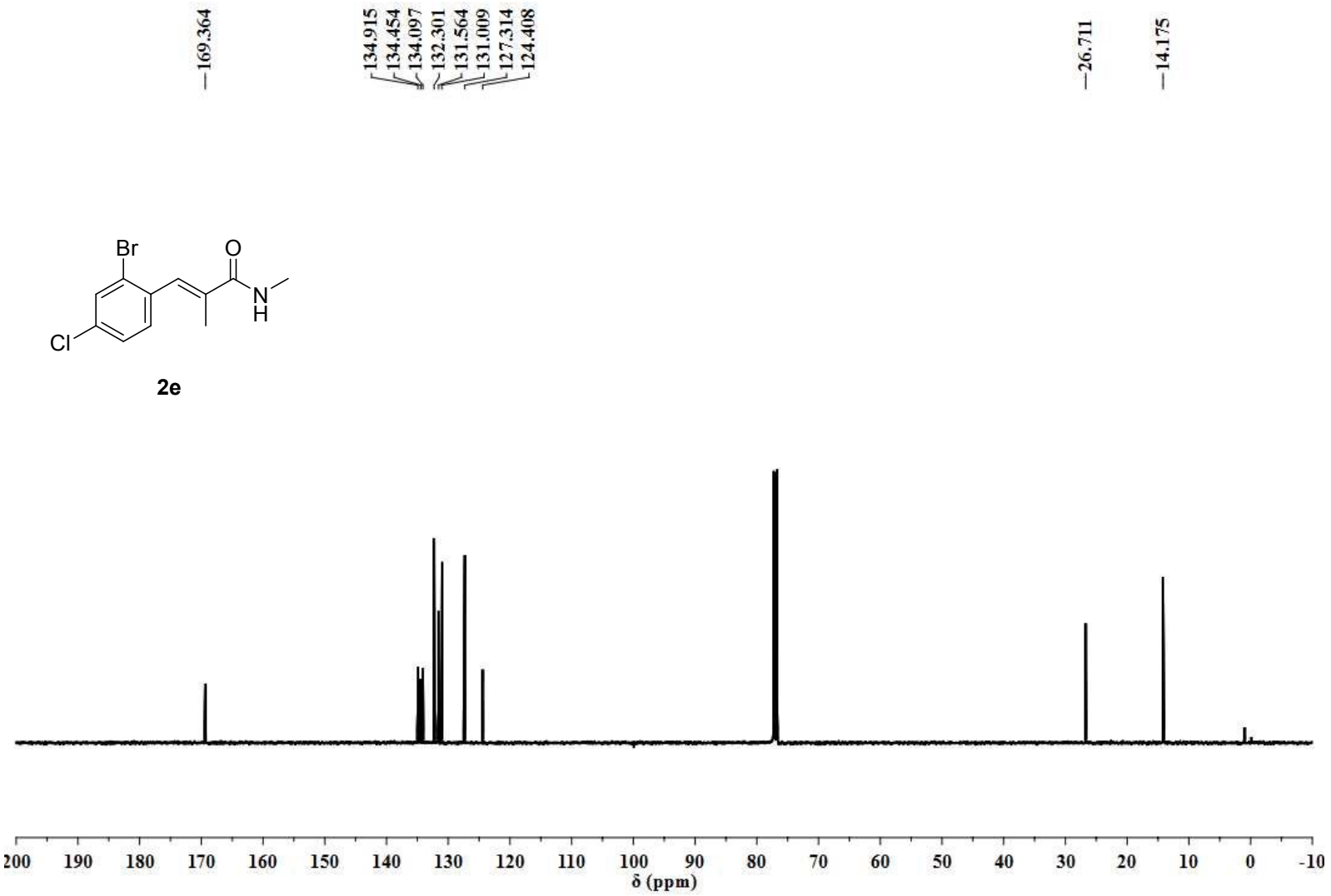
146.849
134.864
130.651
129.602
129.073
127.436
126.438
123.450
121.400
120.828
119.350
117.300
26.570
14.176
OCF3
O
N
H
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

ZBW-WZ-864-F



2d


7.610
7.606
7.302
7.298
7.283
6.201
2.947
2.937
1.949
1.947
Br
O
N
H
Cl
2e
1.00
1.06
1.07
1.09
1.01
3.05
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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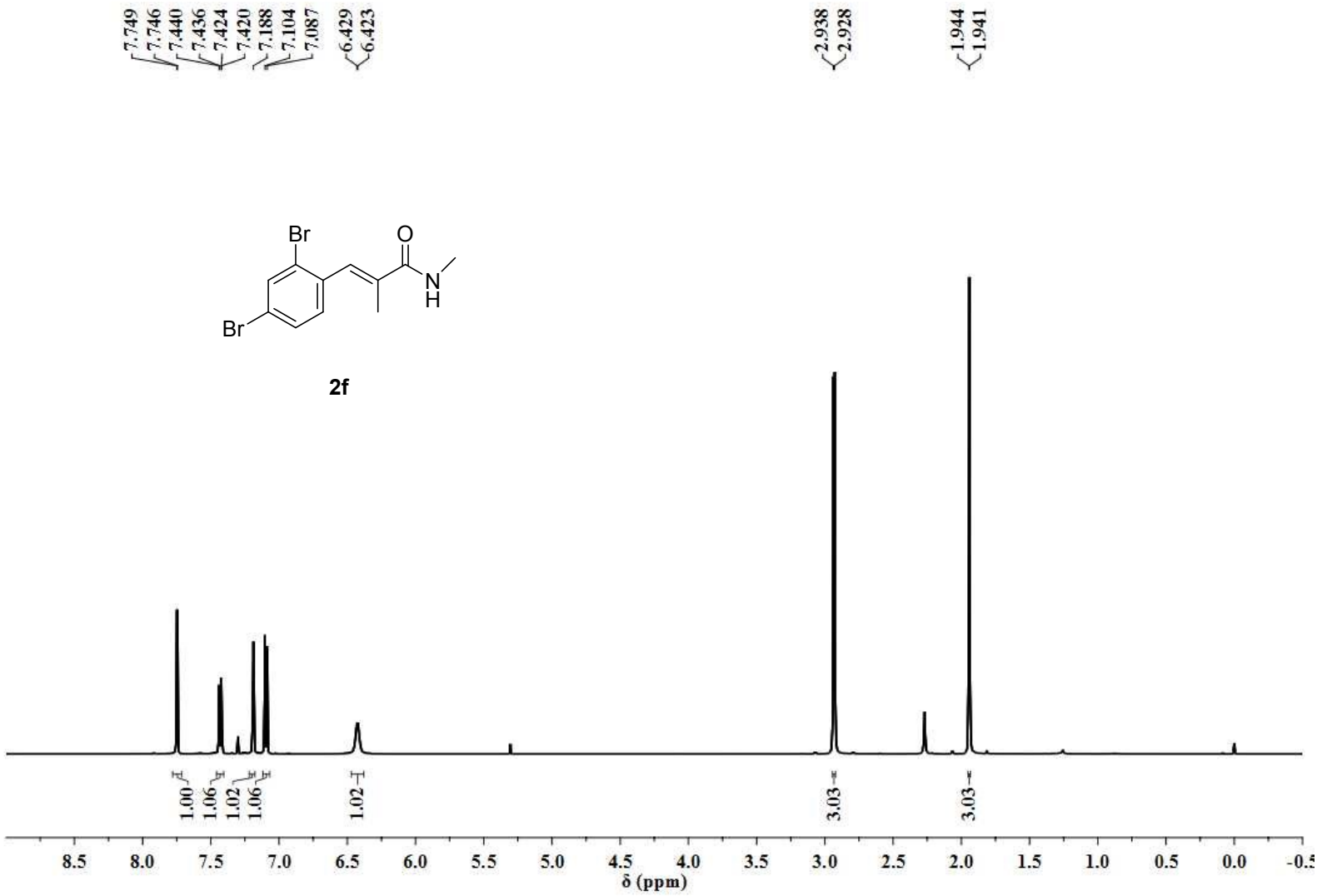
134.915
134.454
134.097
132.301
131.564
131.009
127.314
124.408
26.711
14.175
Br
O
N
H
Cl
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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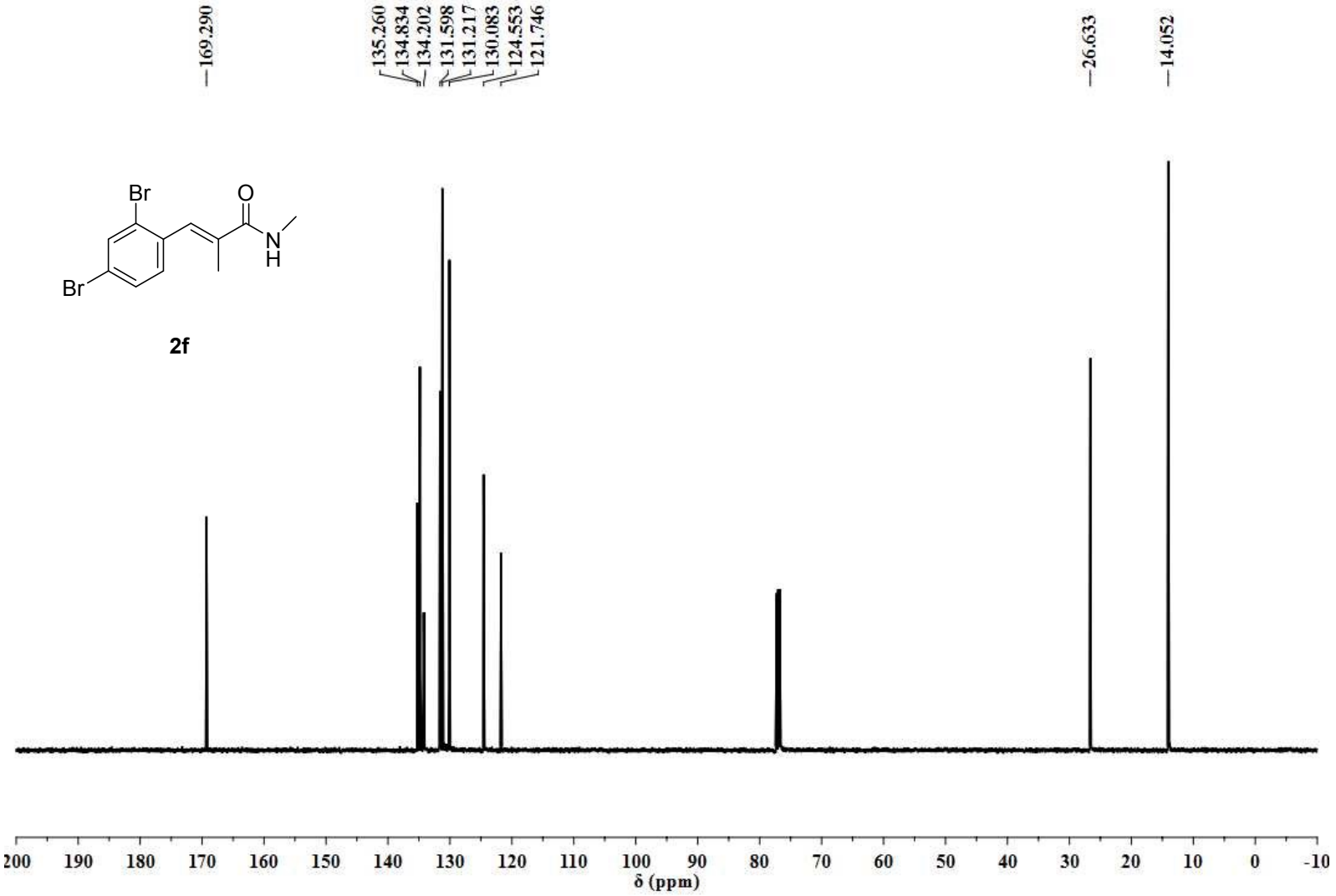
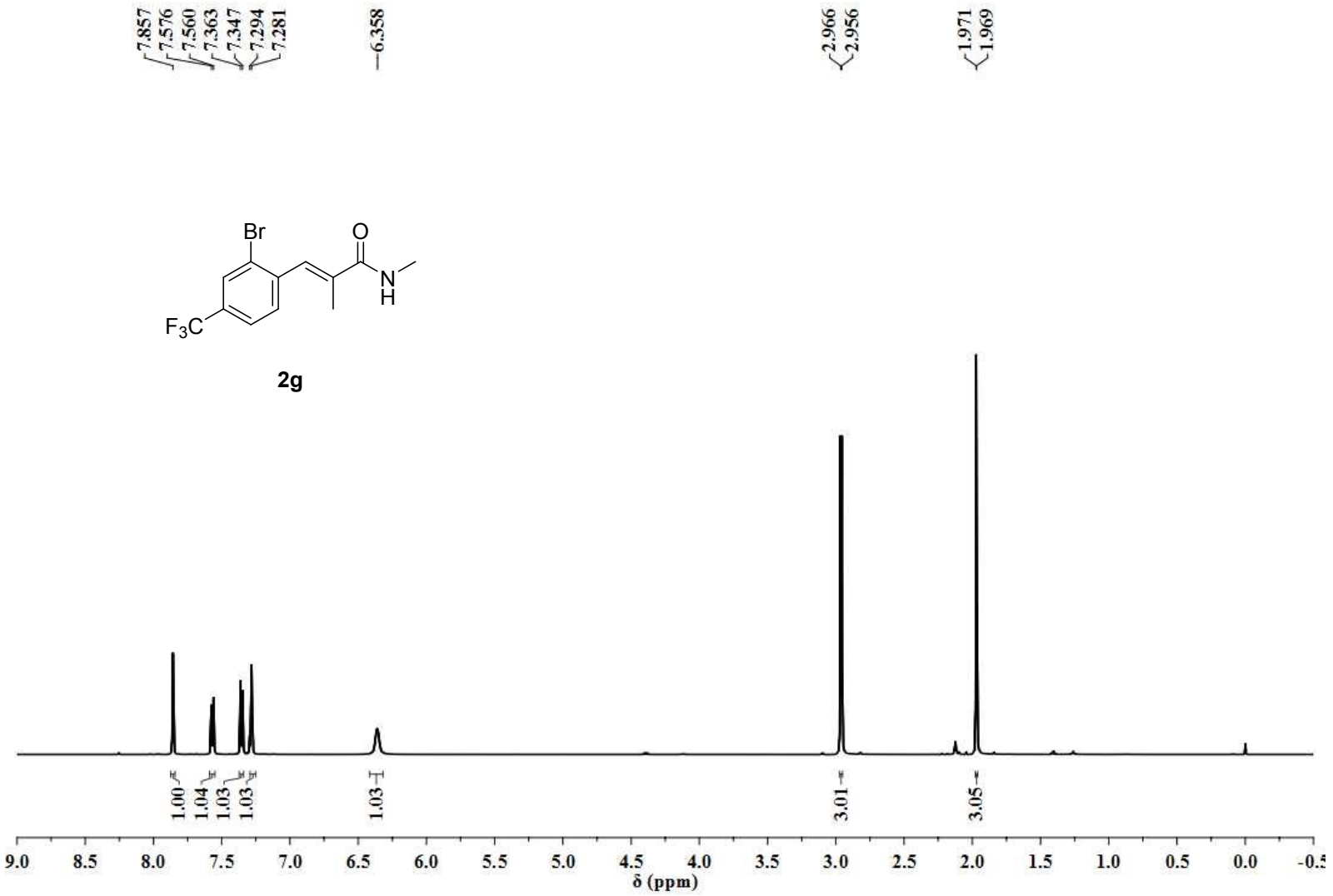
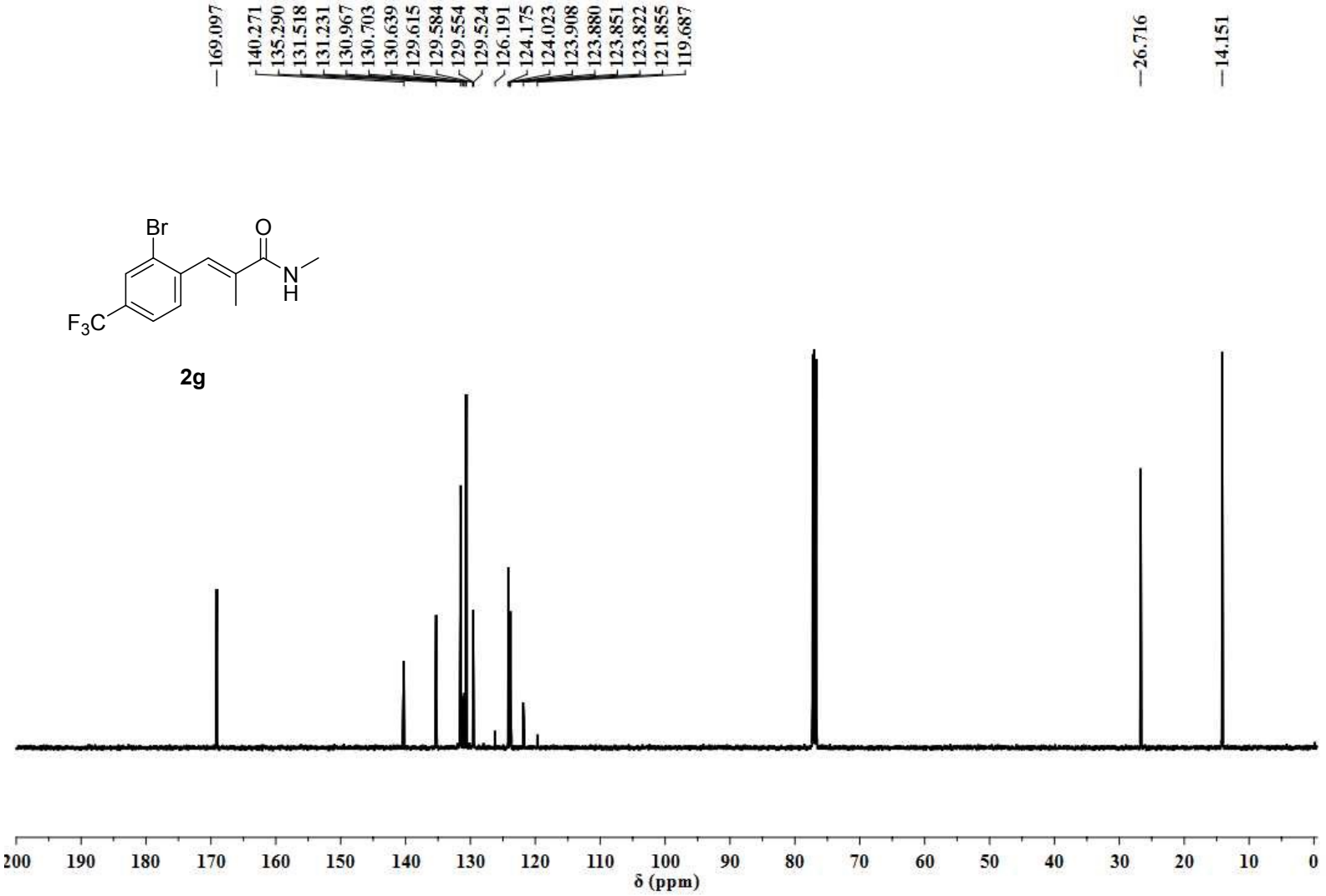
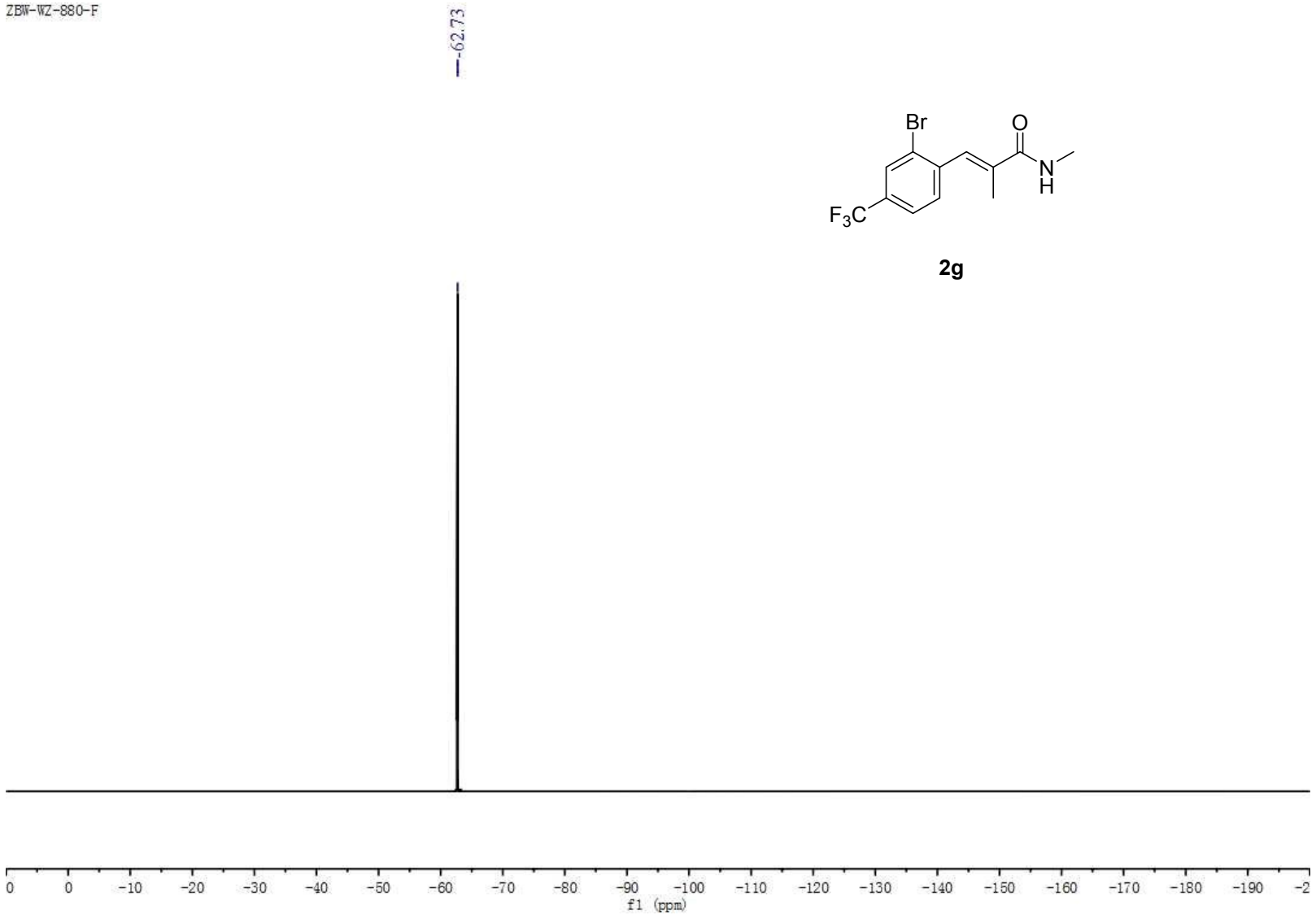
7.746
7.440
7.436
7.424
7.420
7.188
7.104
7.087
6.429
6.423
2.938
2.928
1.944
1.941
Br
O
N
H
Br
1.00
1.06
1.02
1.06
1.02
3.03
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

2f

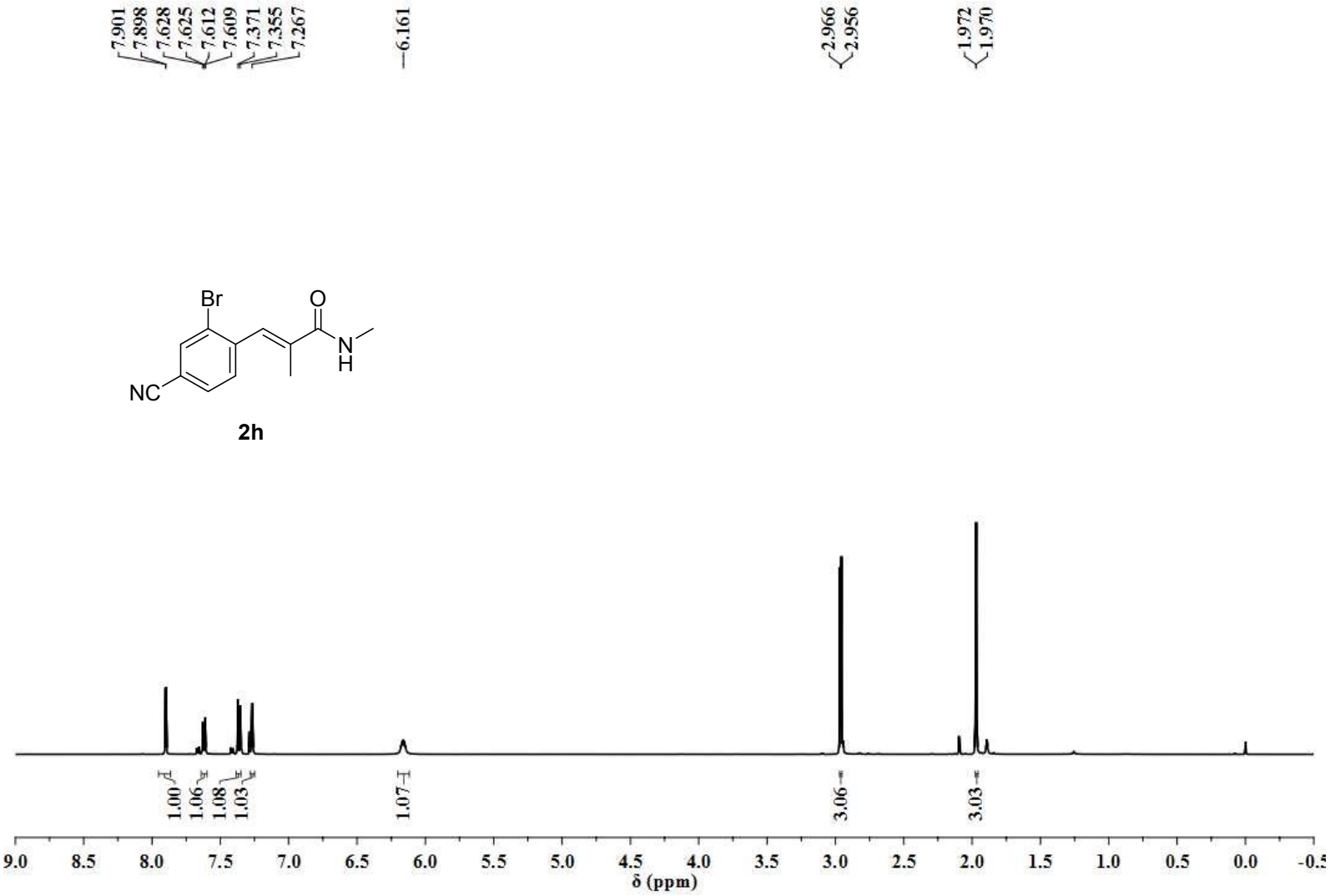

169.290
135.260
134.834
134.202
131.598
131.217
130.083
124.553
121.746
26.633
14.052
Br
O
N
H
Br
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.857
7.576
7.560
7.363
7.347
7.294
7.281
6.358
2.966
2.956
1.971
1.969
Br
O
N
H
F3C
2g
1.00
1.04
1.03
1.03
1.03
3.01
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


169.097
140.271
135.290
131.518
131.231
130.967
130.703
130.639
129.615
129.584
129.554
129.524
126.191
124.175
124.023
123.908
123.880
123.851
123.822
121.855
119.687
26.716
14.151
Br
O
N
H
F3C
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


ZBW-WZ-880-F
-62.73
Br
O
N
H
F3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

2g


7.901
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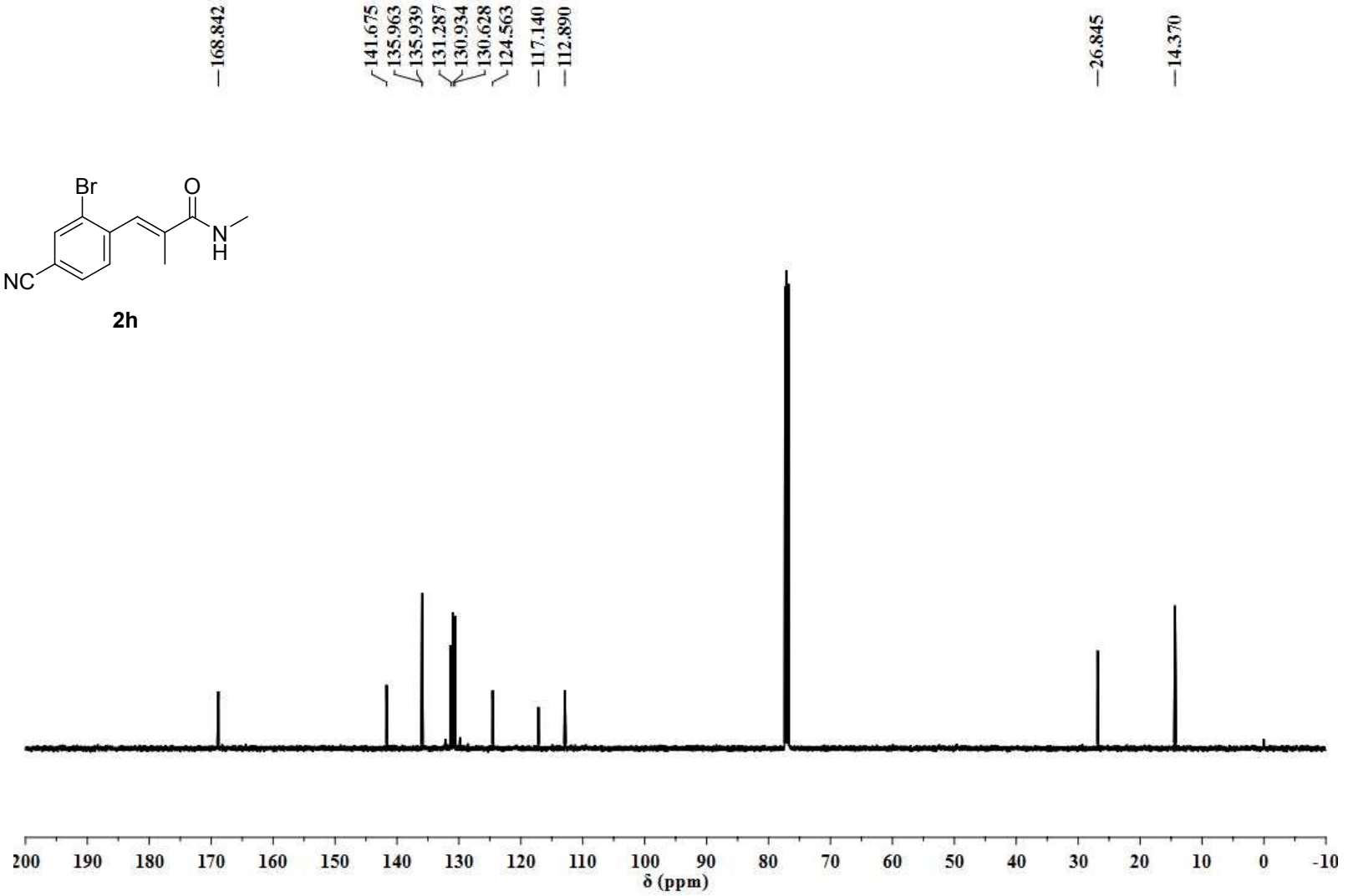
7.625
7.612
7.609
7.371
7.355
7.267
6.161
2.966
2.956
1.972
1.970
Br
O
N
H
NC
2h
1.00
1.06
1.08
1.03
1.07
3.06
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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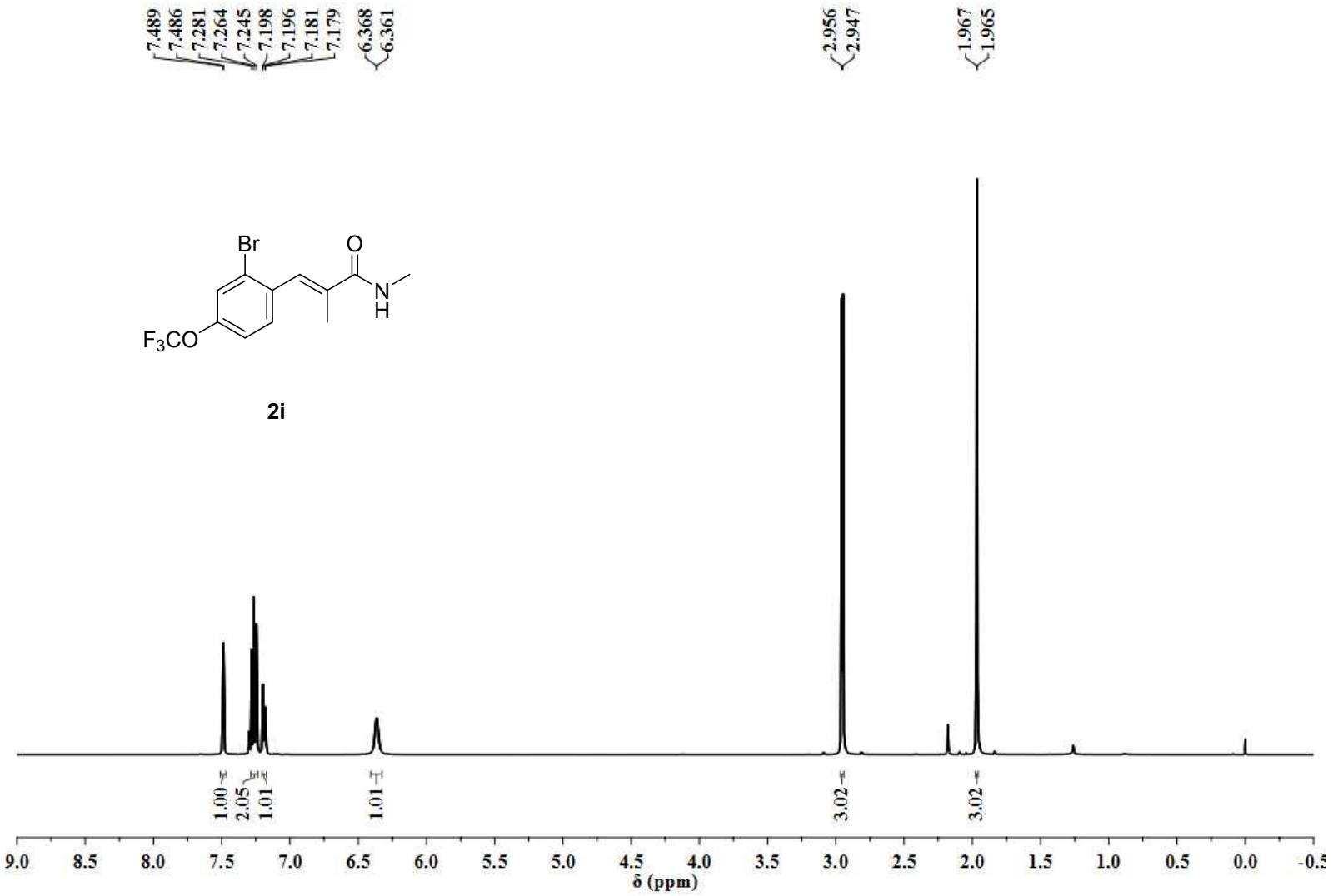
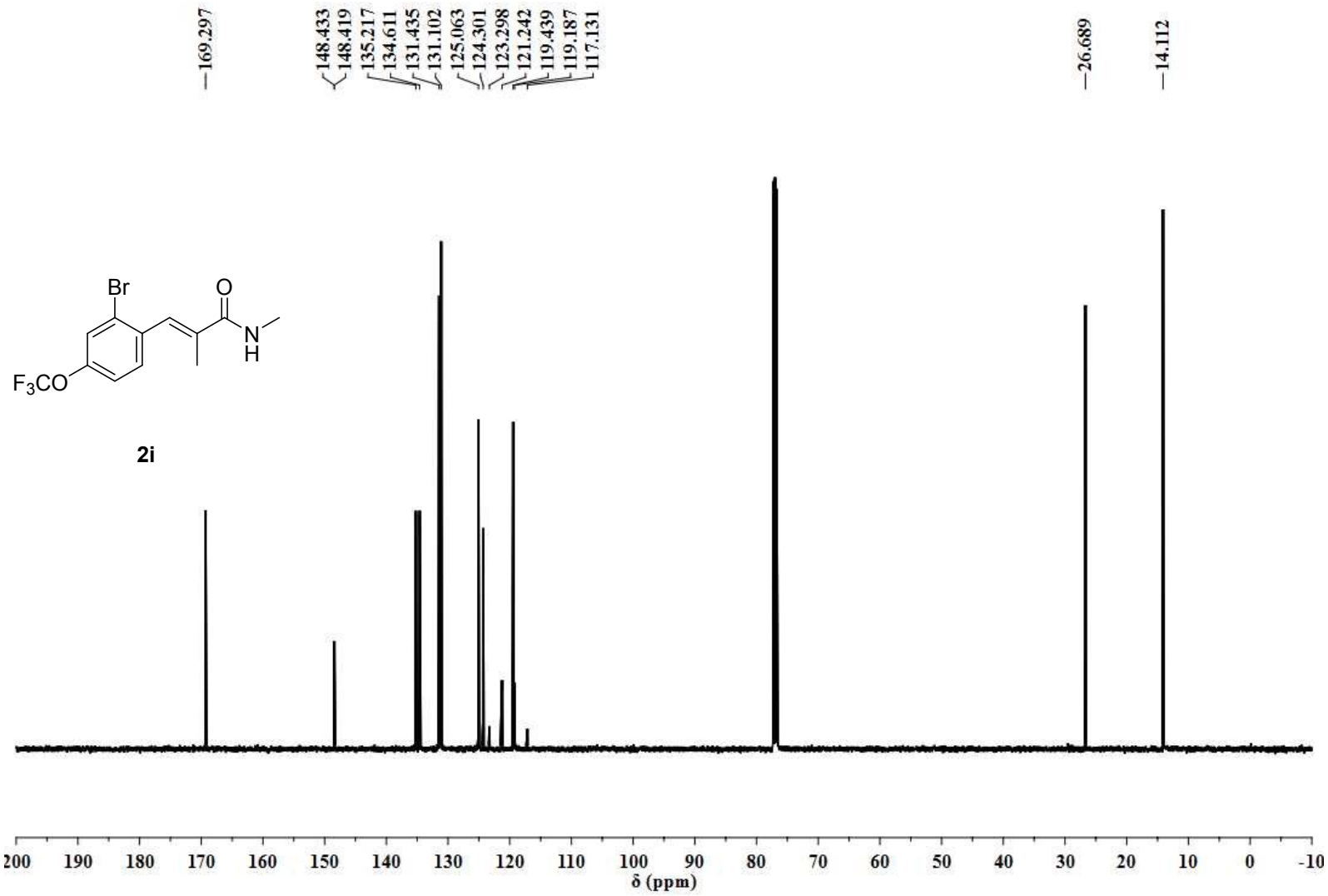
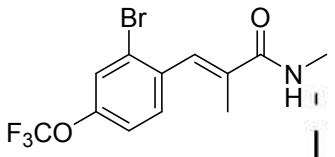
135.963
135.939
131.287
130.934
130.628
124.563
117.140
112.890
26.845
14.370
Br
O
N
H
NC
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


7.489
7.486
7.281
7.264
7.245
7.198
7.196
7.181
7.179
6.368
6.361
2.956
2.947
1.967
1.965
Br
O
N
H
F3CO
1.00
2.05
1.01
1.01
3.02
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

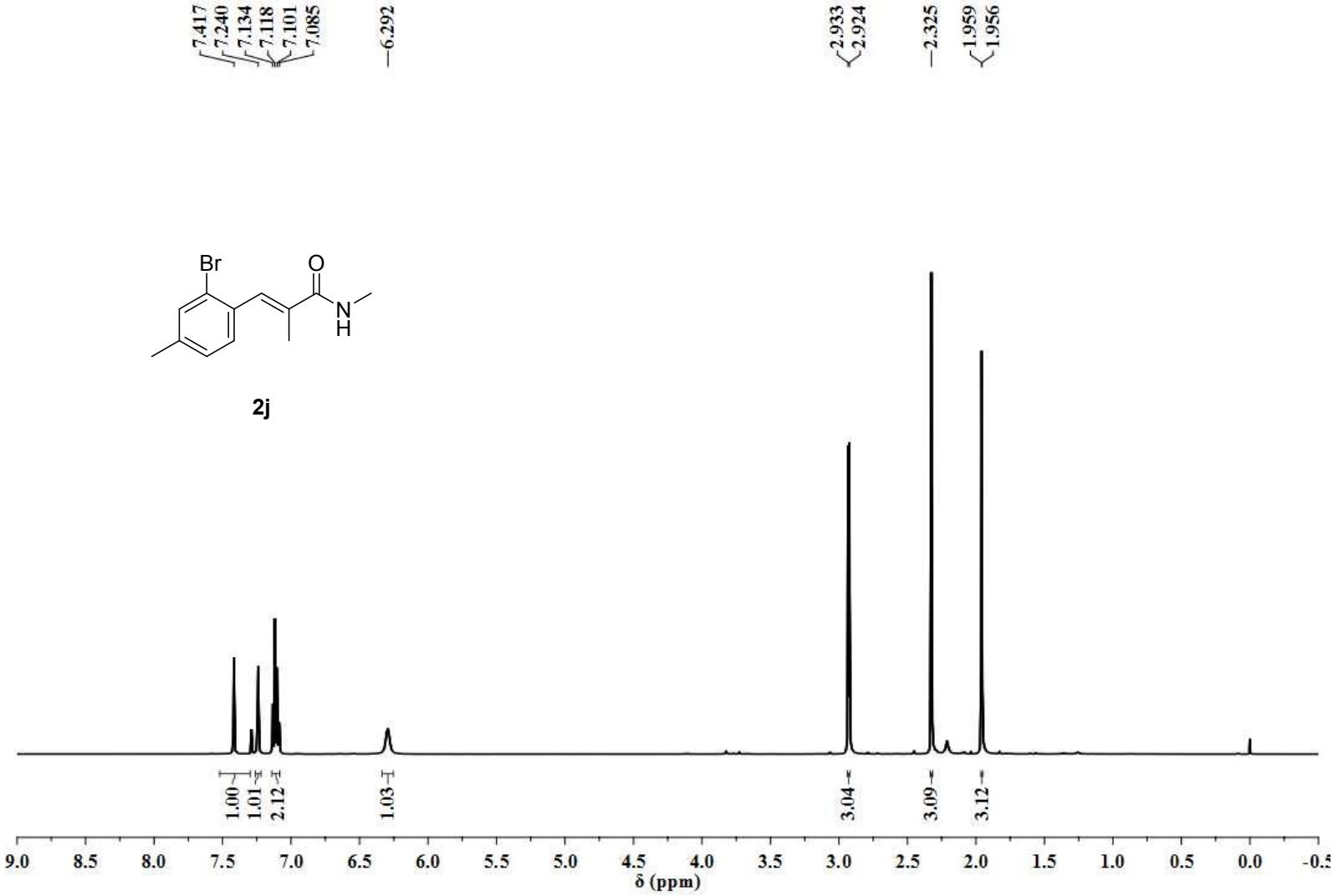
2i

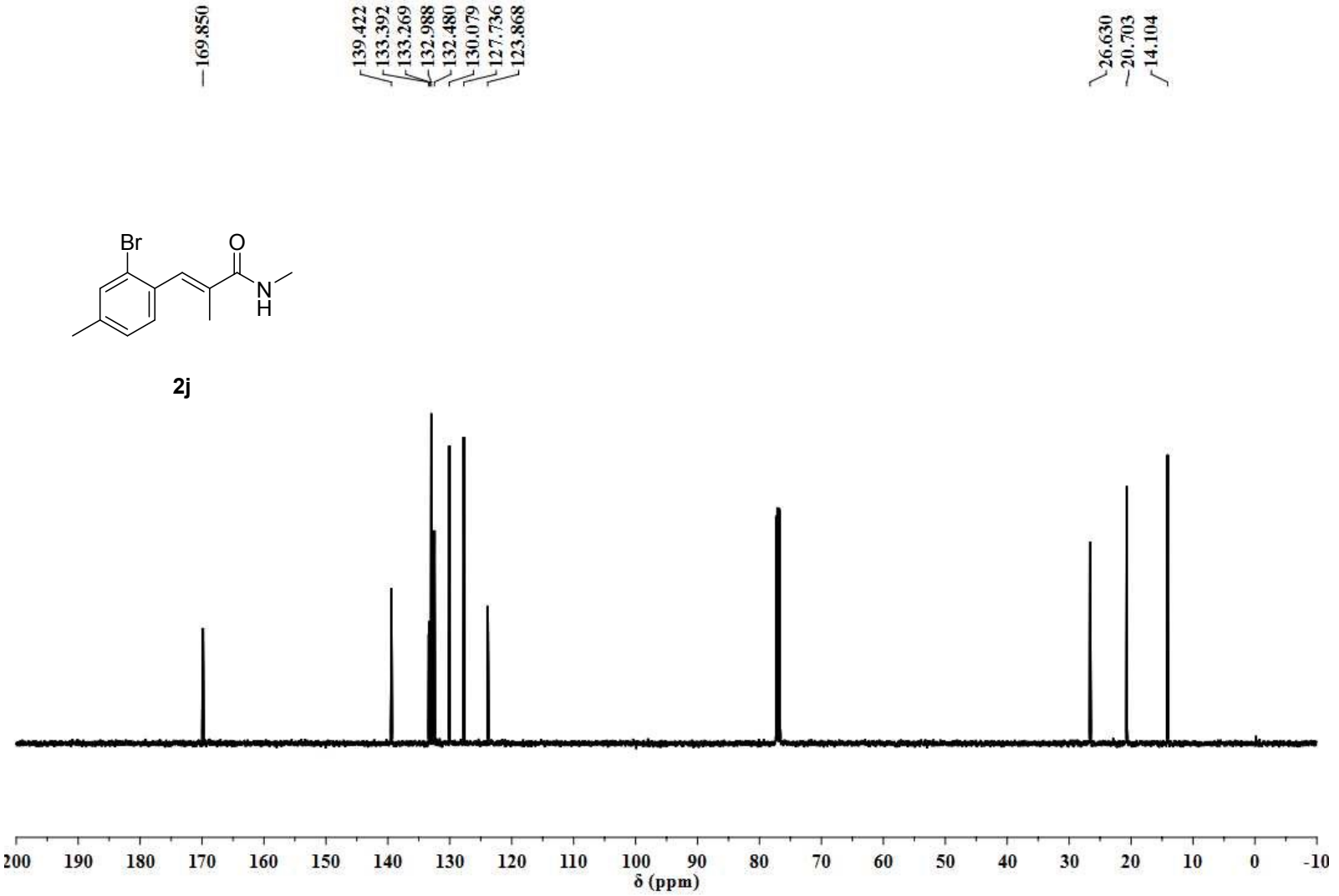

169.297
148.433
148.419
135.217
134.611
131.435
131.102
125.063
124.301
123.298
121.242
119.439
119.187
117.131
26.689
14.112
Br
O
N
H
F3CO
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

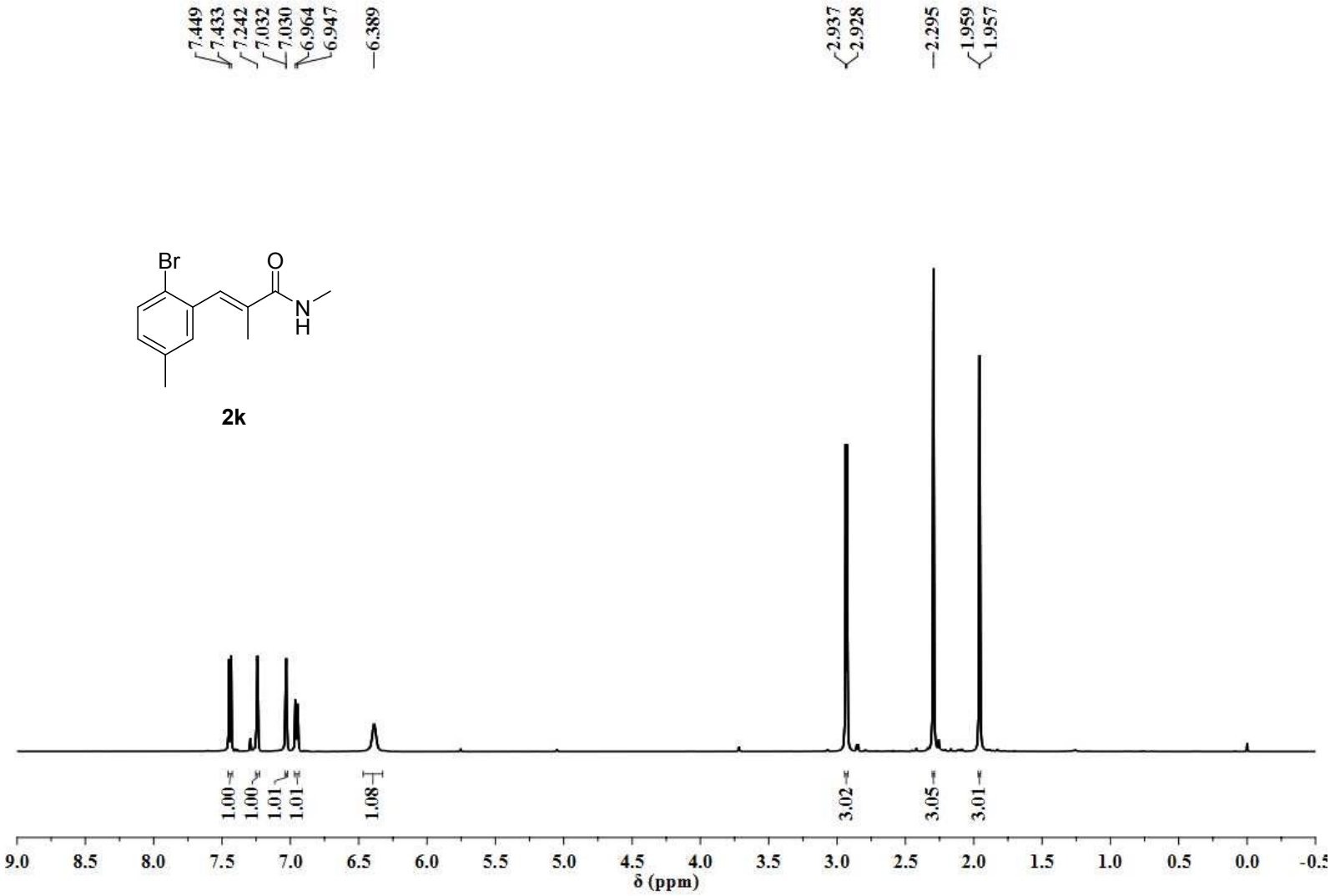
ZBW-WZ-964-F

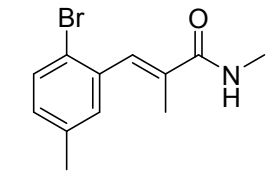


2i


7.417
7.240
7.134
7.118
7.101
7.085
6.292
2.933
2.924
2.325
1.959
1.956
Br
O
N
H
2j
1.00
1.01
2.12
1.03
3.04
3.09
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

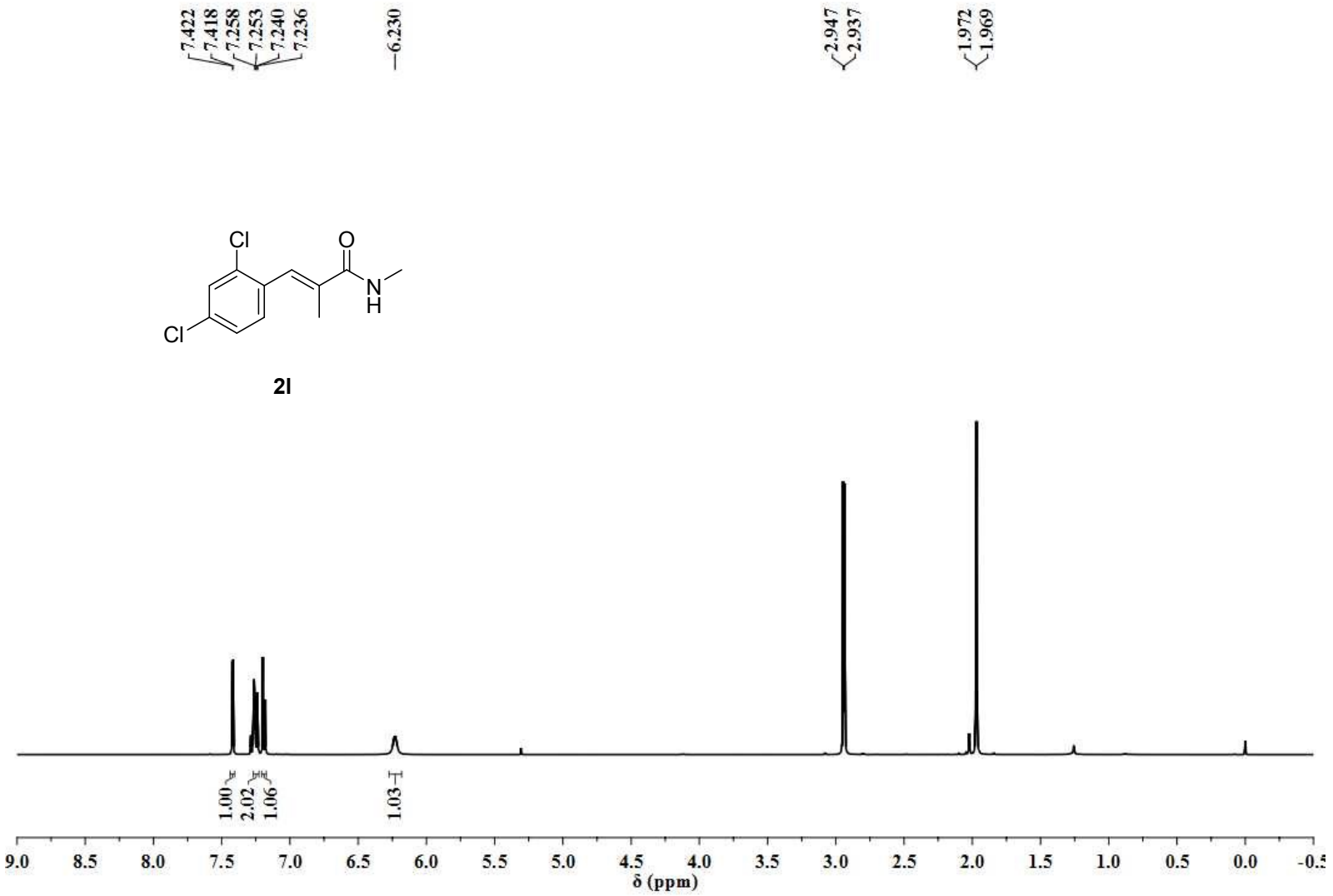

169.850
139.422
133.392
133.269
132.988
132.480
130.079
127.736
123.868
26.630
20.703
14.104
Br
O
N
H
2j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


7.449
7.433
7.242
7.032
7.030
6.964
6.947
6.389
2.937
2.928
2.295
1.959
1.957
Br
O
N
H
2k
1.00
1.00
1.01
1.01
1.08
3.02
3.05
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

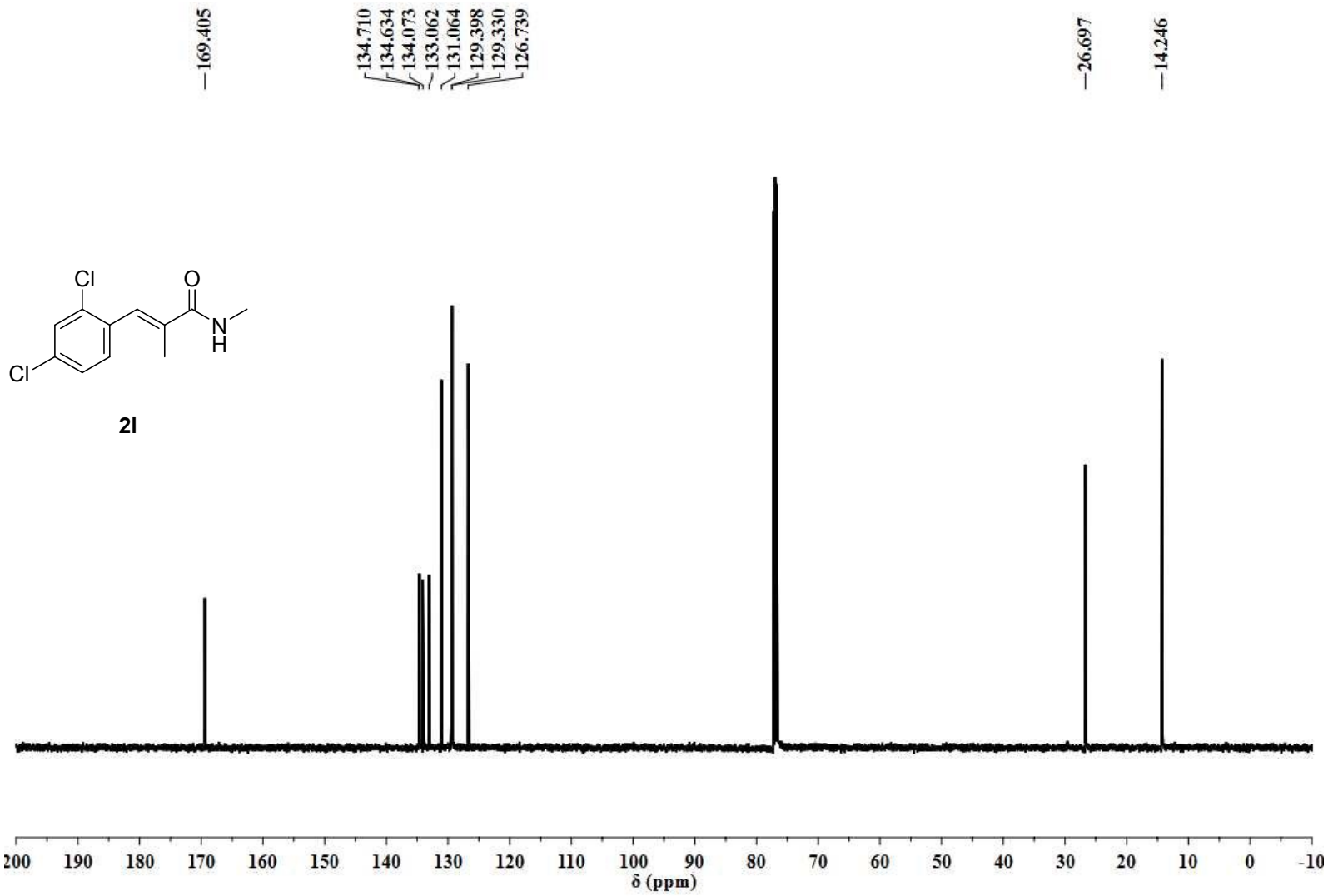

Br
O
N
H

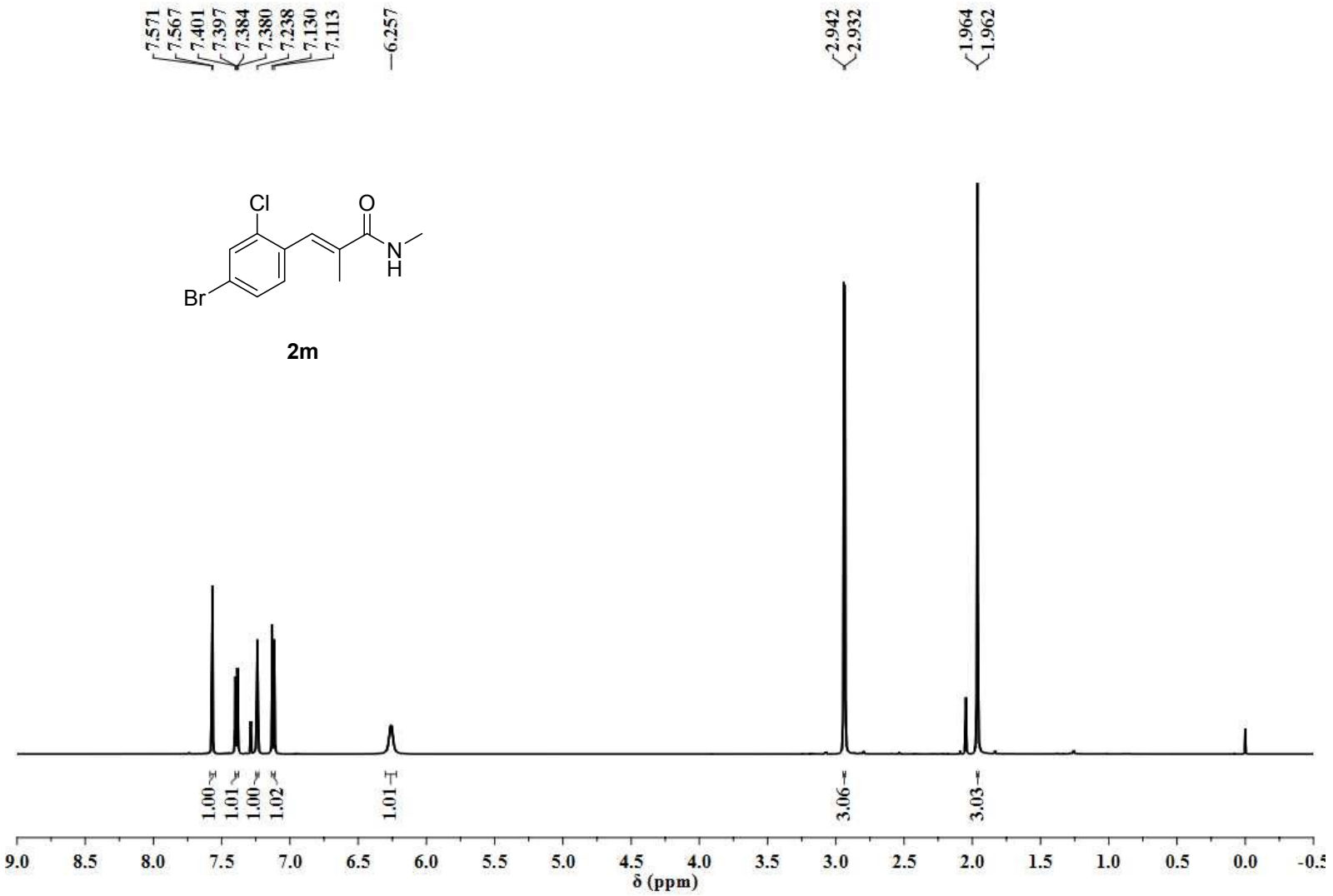
2k

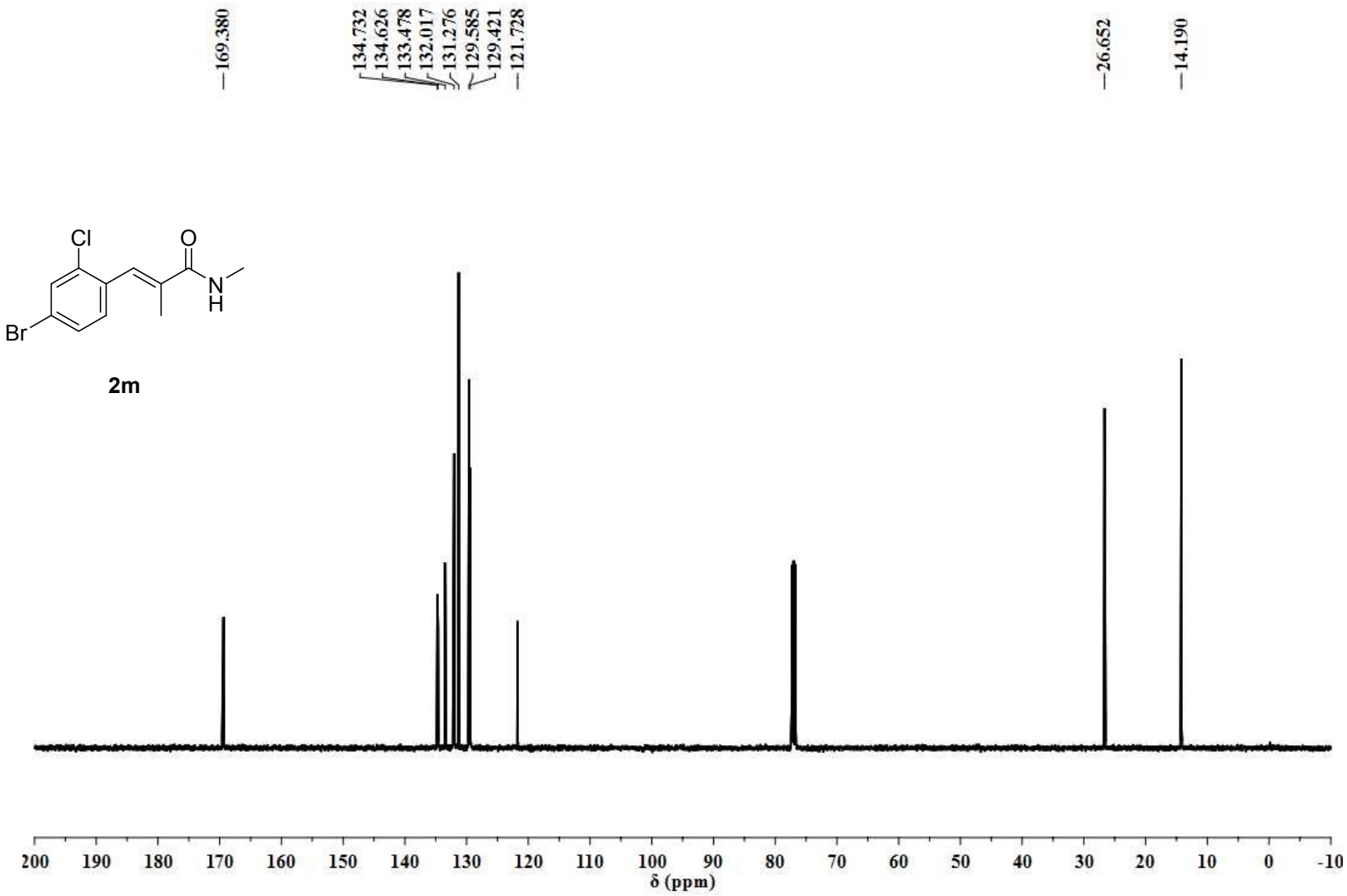
169.697
136.744
135.995
133.540
132.658
132.164
130.897
129.858
120.536
26.604
20.767
14.072
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

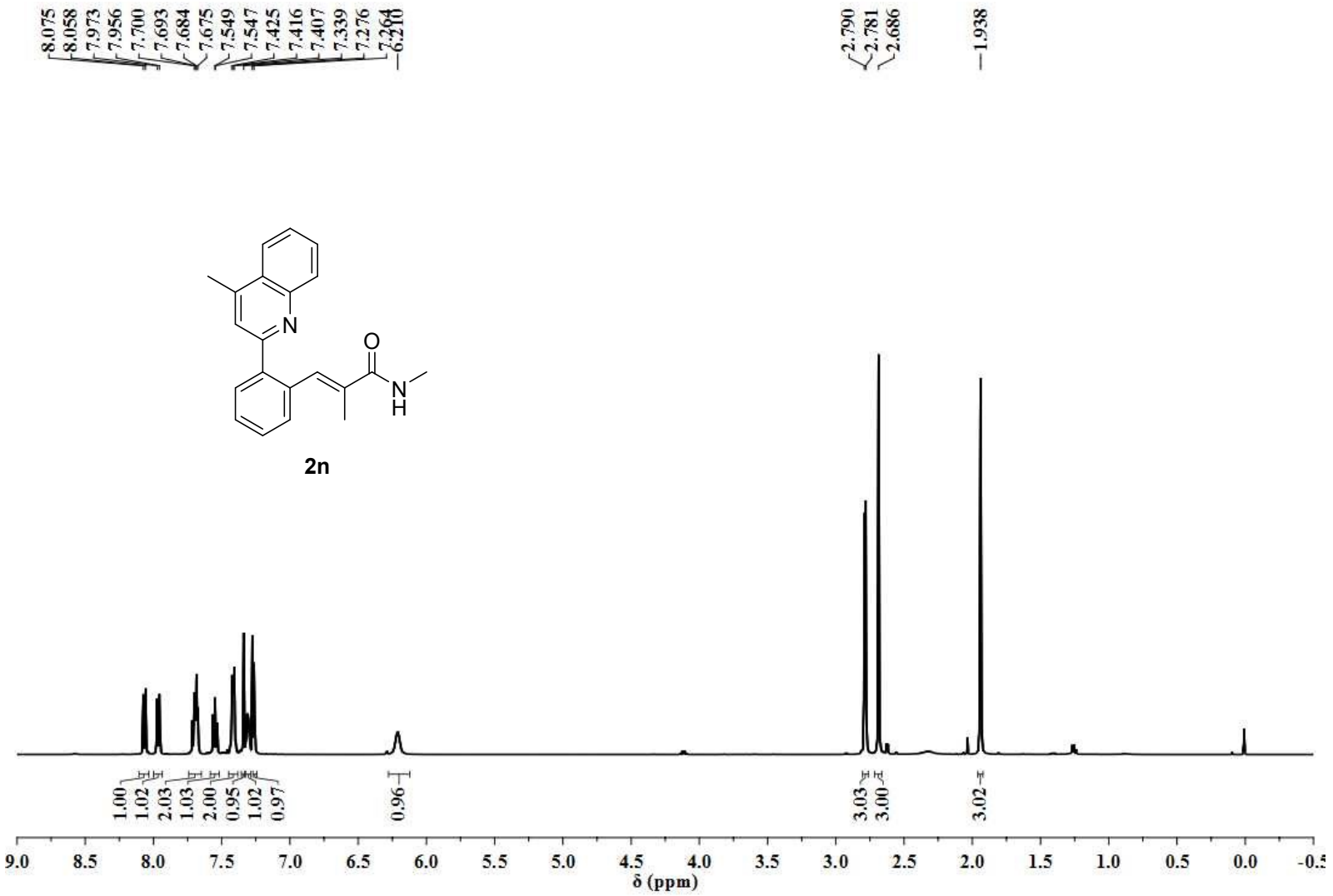

7.422
7.418
7.258
7.253
7.240
7.236
6.230
2.947
2.937
1.972
1.969
Cl
O
N
H
Cl
1.00
2.02
1.06
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

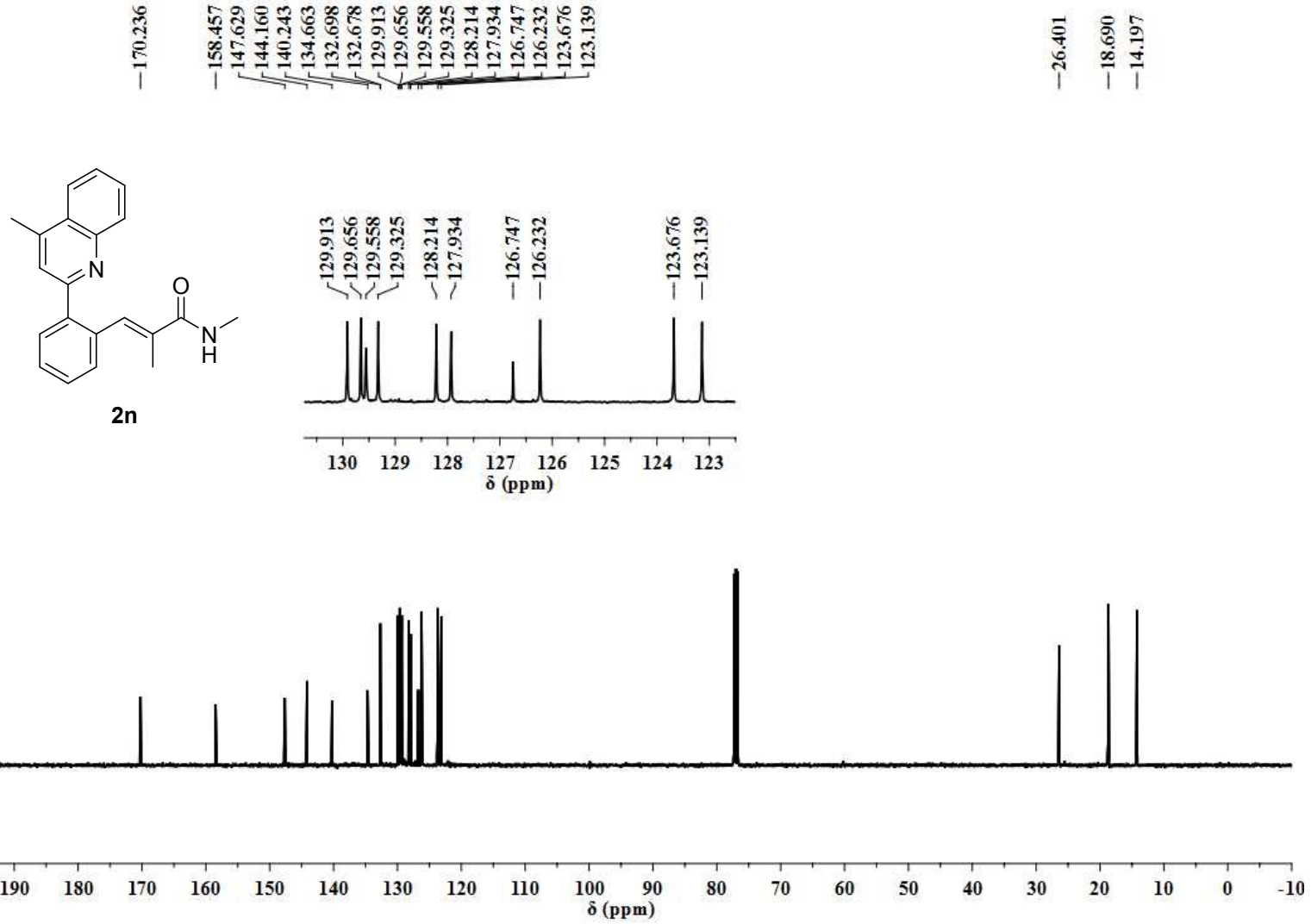
2l

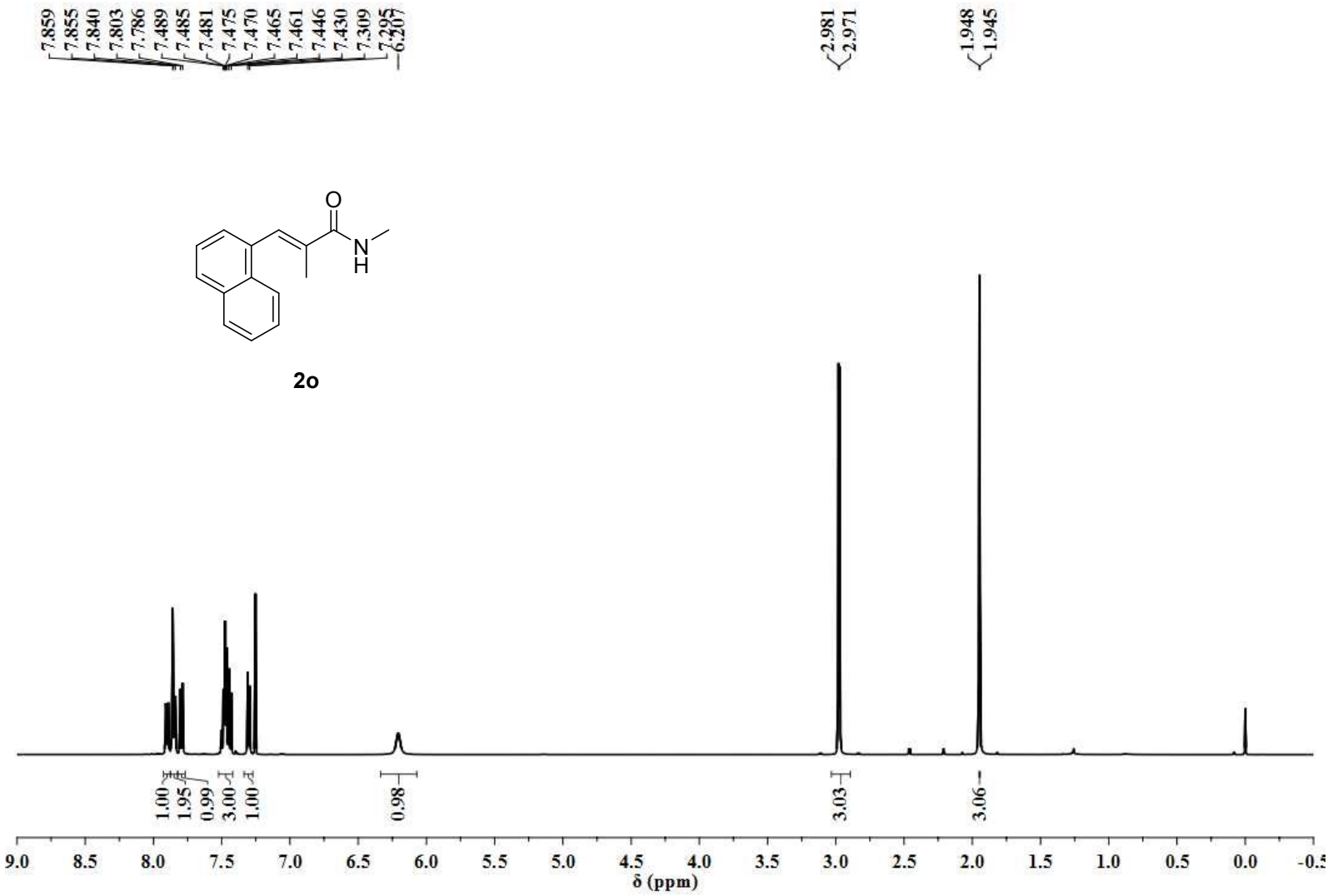

169.405
134.710
134.634
134.073
133.062
131.064
129.398
129.330
126.739
26.697
14.246
Cl
O
N
H
Cl
2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.571
7.567
7.401
7.397
7.384
7.380
7.238
7.130
7.113
6.257
2.942
2.932
1.964
1.962
Cl
O
N
H
Br
2m
1.00
1.01
1.00
1.02
1.01
3.06
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

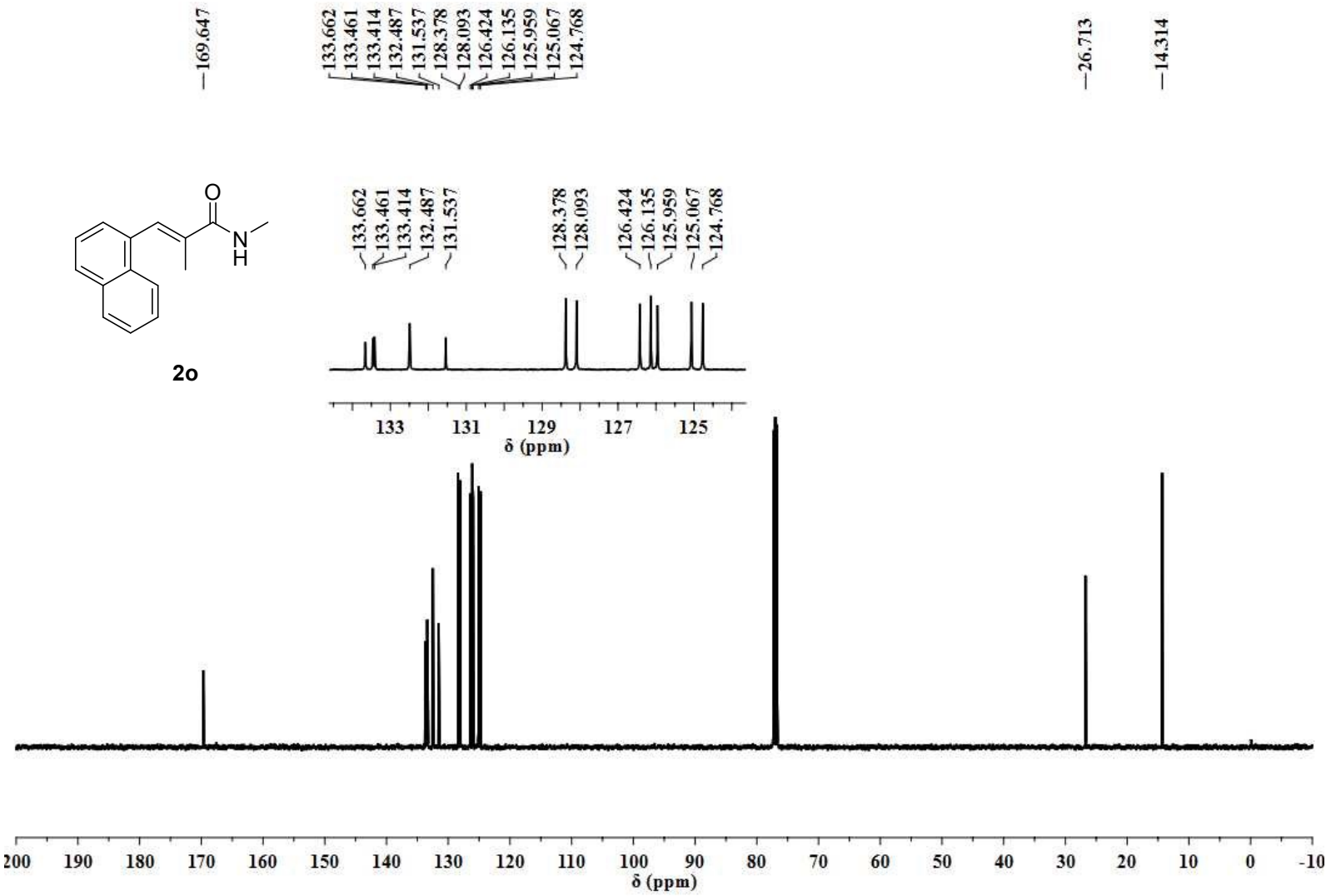

169.380
134.732
134.626
133.478
132.017
131.276
129.585
129.421
121.728
26.652
14.190
Cl
O
N
H
Br
2m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

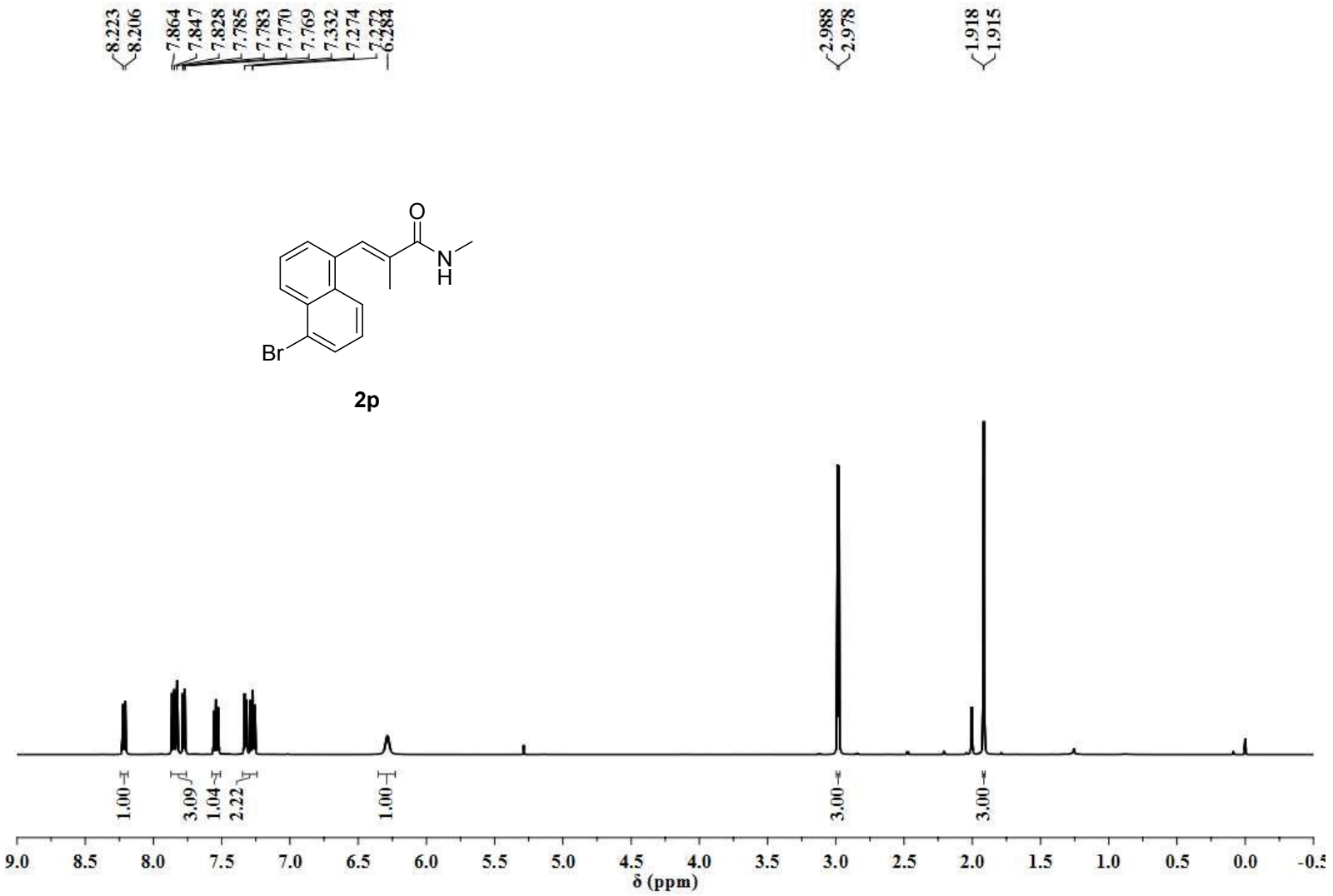

8.075
8.058
7.973
7.956
7.700
7.693
7.684
7.675
7.549
7.547
7.425
7.416
7.407
7.339
7.276
6.210
2.790
2.781
2.686
1.938
N
O
N
H
2n
1.00
1.02
2.03
1.03
2.00
0.95
1.02
0.97
0.96
3.03
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


170.236
158.457
147.629
144.160
140.243
134.663
132.698
132.678
129.913
129.656
129.558
129.325
128.214
127.934
126.747
126.232
123.676
123.139
26.401
18.690
14.197
N
O
N
H
2n
130
129
128
127
126
125
124
123
δ (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

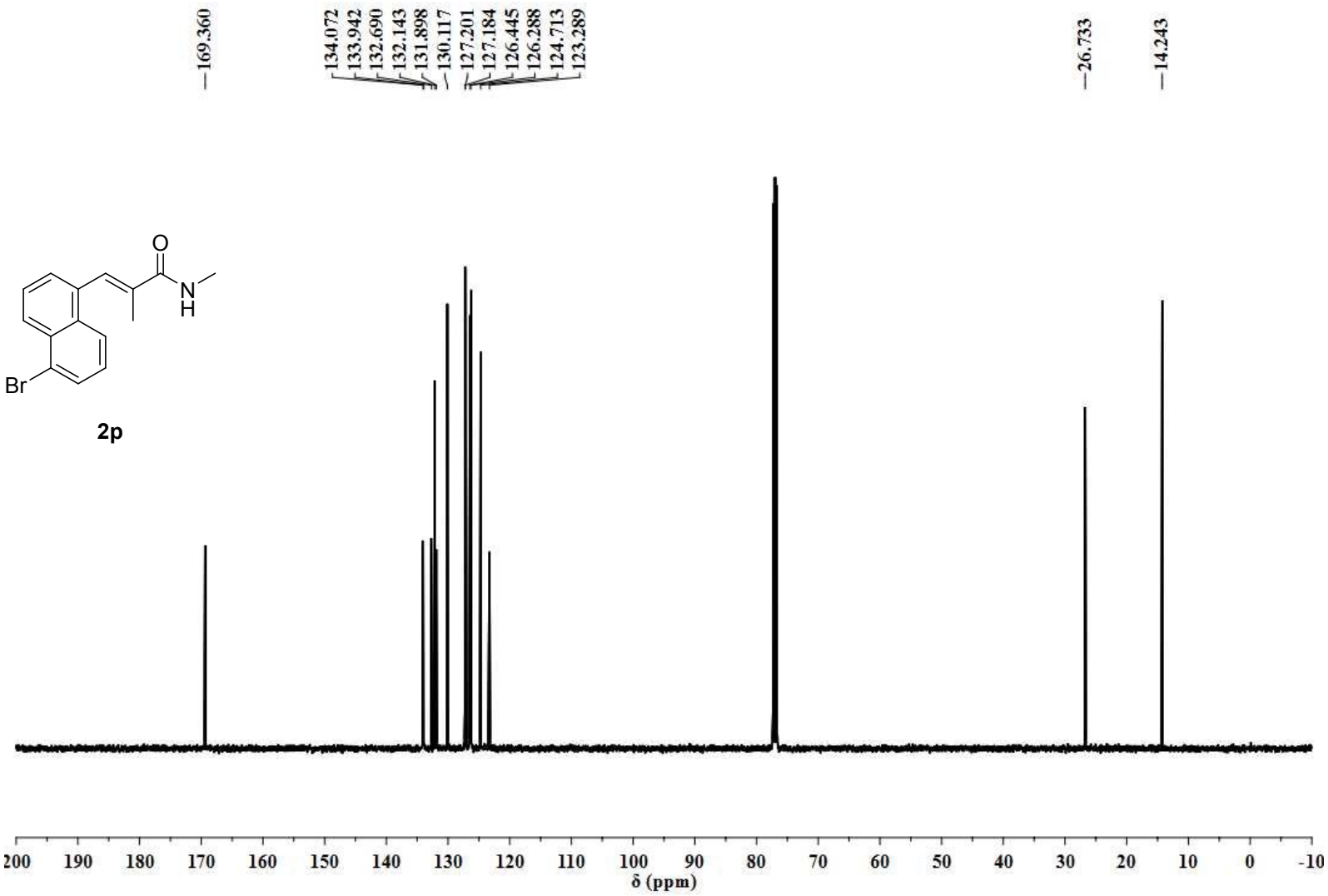

7.859
7.855
7.840
7.803
7.786
7.489
7.485
7.481
7.475
7.470
7.465
7.461
7.446
7.430
7.309
7.295
7.207
2.981
2.971
1.948
1.945
O
N
H
1.00
1.95
0.99
3.00
1.00
0.98
3.03
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

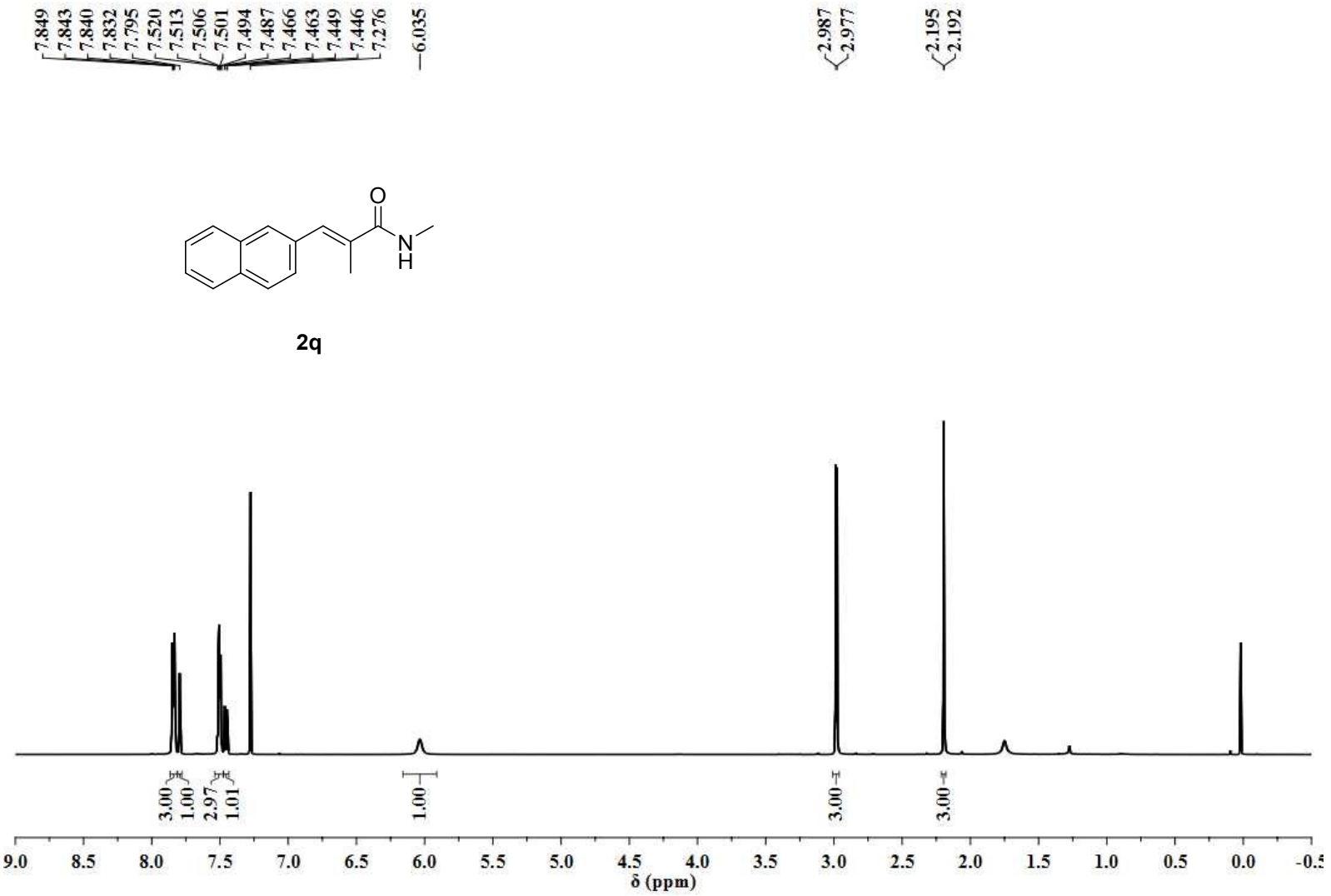
2o


169.647
133.662
133.461
133.414
132.487
131.537
128.378
128.093
126.424
126.135
125.959
125.067
124.768
26.713
14.314
O
N
H
2o
δ (ppm)
δ (ppm)

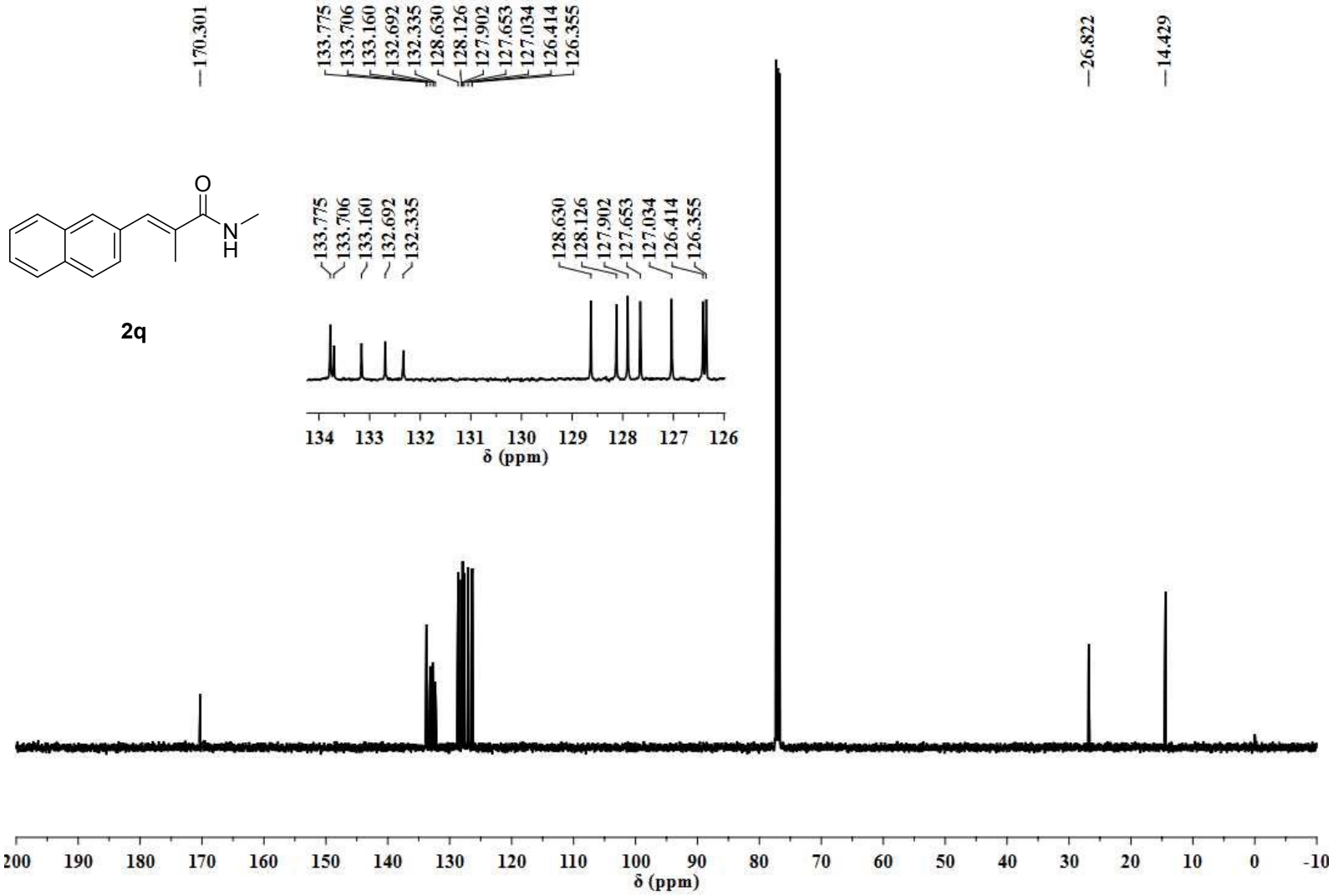

8.223
8.206
7.864
7.847
7.828
7.785
7.783
7.770
7.769
7.332
7.274
7.272
6.284
2.988
2.978
1.918
1.915
O
N
H
Br
1.00
3.09
1.04
2.22
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

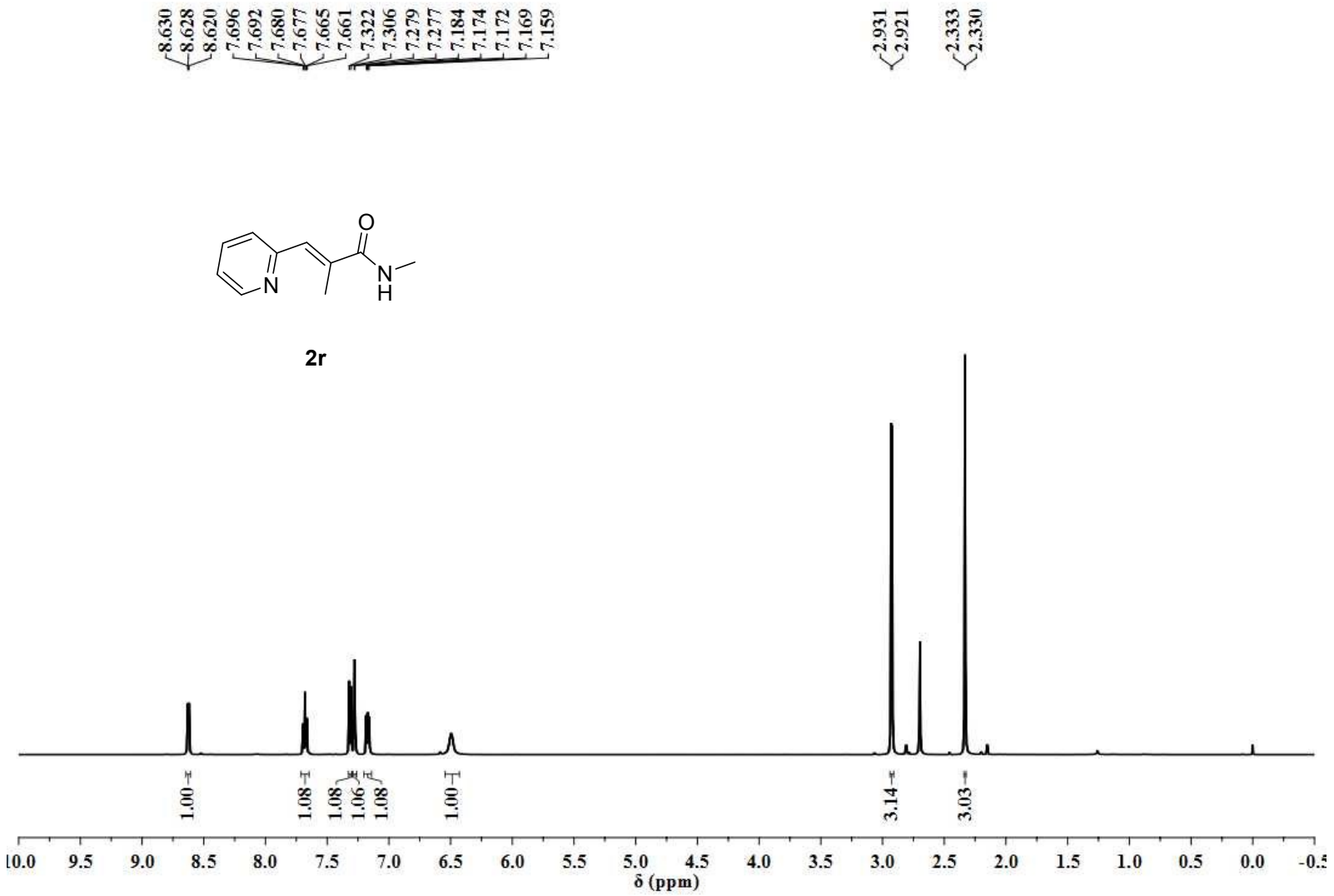
2p

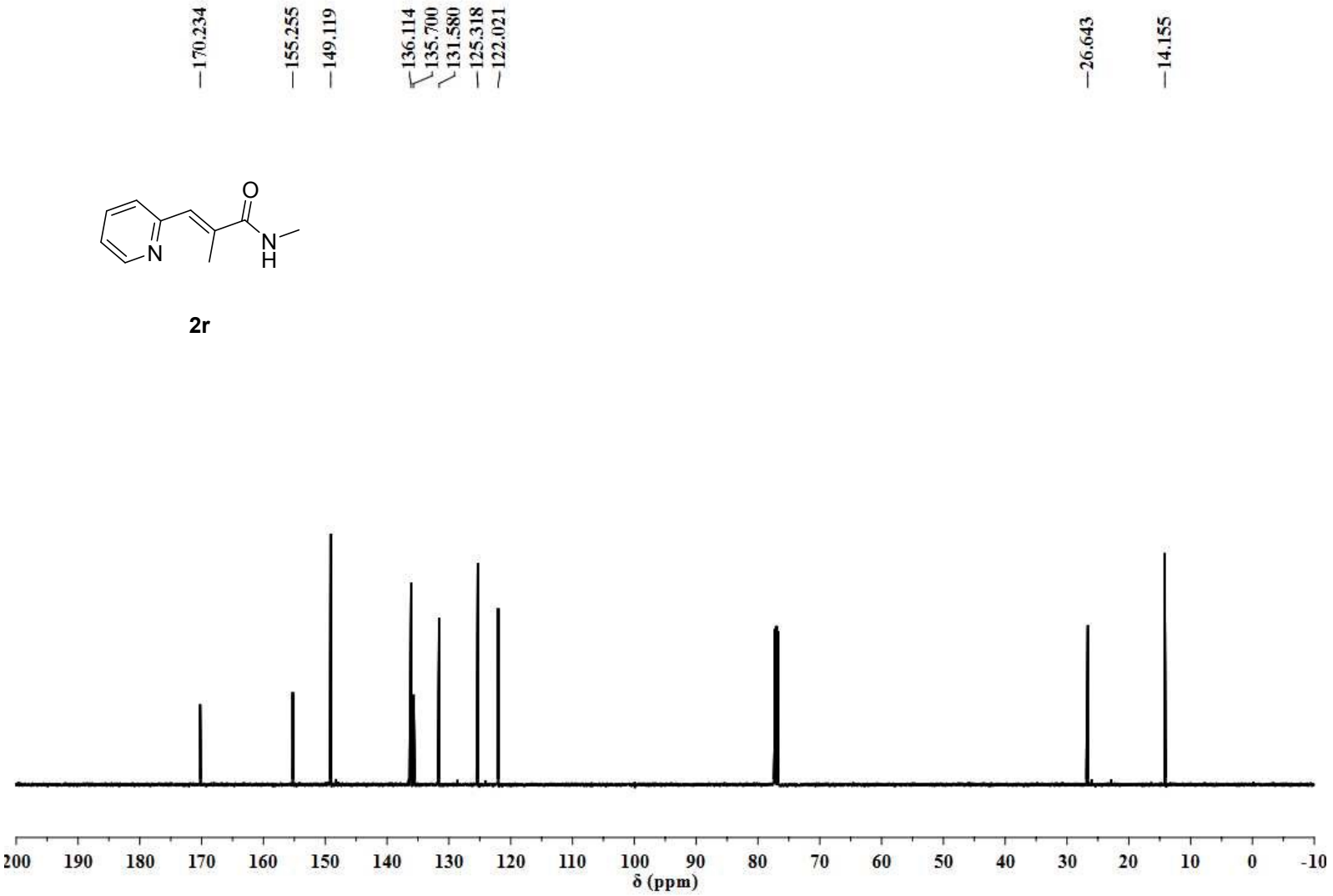

169.360
134.072
133.942
132.690
132.143
131.898
130.117
127.201
127.184
126.445
126.288
124.713
123.289
26.733
14.243
O
N
H
Br
2p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


7.849
7.843
7.840
7.832
7.795
7.520
7.513
7.506
7.501
7.494
7.487
7.466
7.463
7.449
7.446
7.276
6.035
2.987
2.977
2.195
2.192
O
N
H
3.00
1.00
2.97
1.01
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

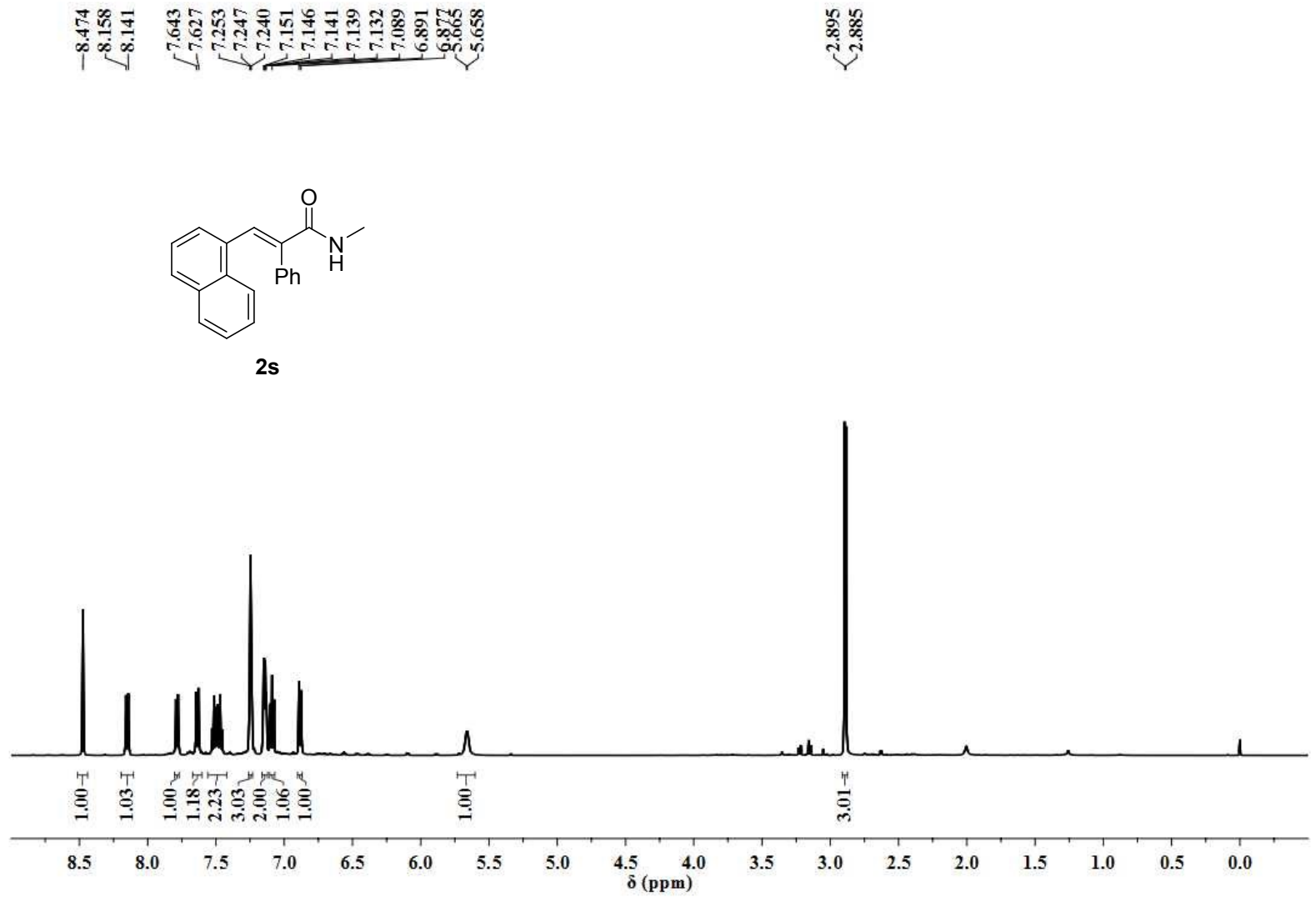
2q


170.301
133.775
133.706
133.160
132.692
132.335
128.630
128.126
127.902
127.653
127.034
126.414
126.355
26.822
14.429
O
N
H
2q
δ (ppm)
δ (ppm)

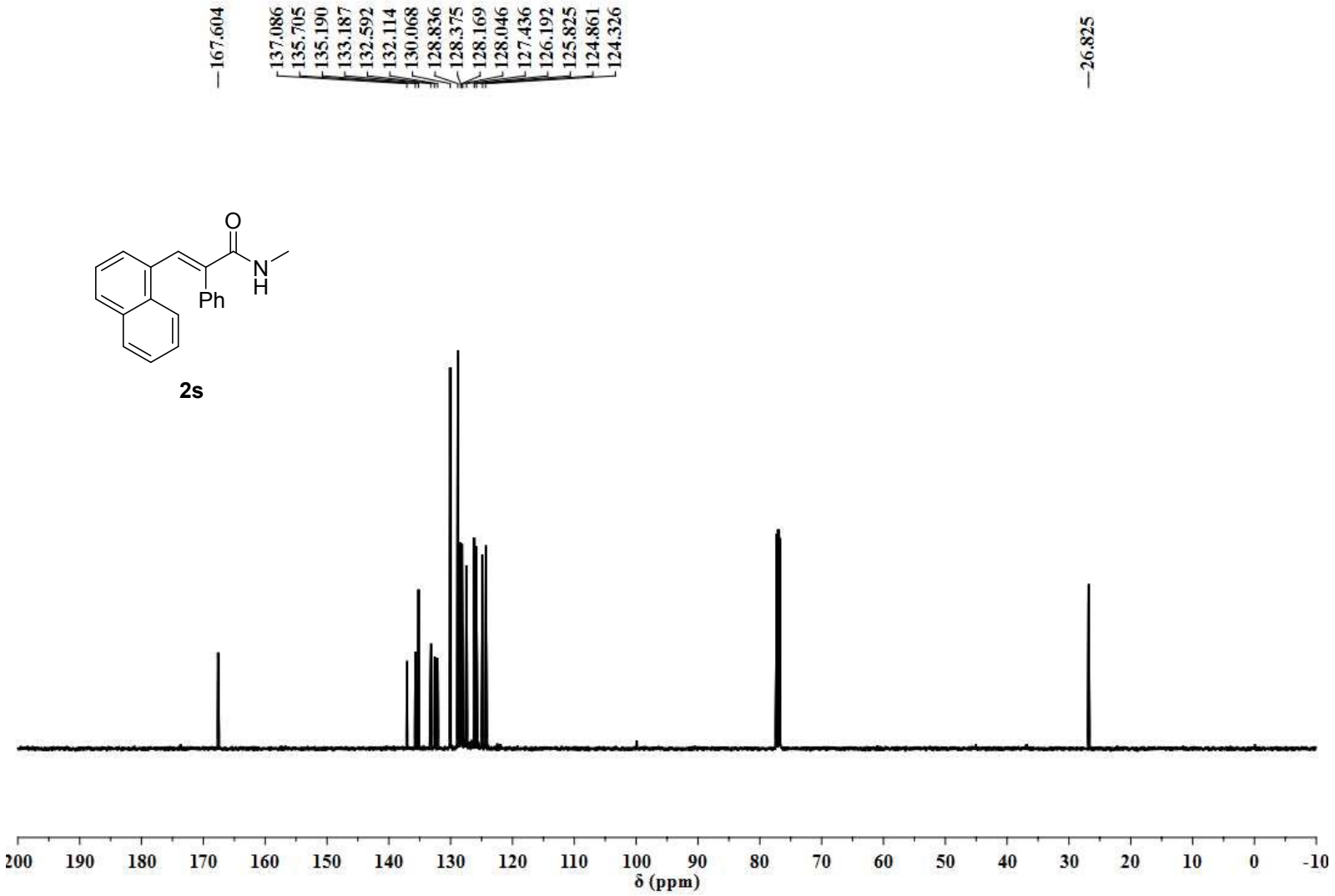

8.630
8.628
8.620
7.696
7.692
7.680
7.677
7.665
7.661
7.322
7.306
7.279
7.277
7.184
7.174
7.172
7.169
7.159
2.931
2.921
2.333
2.330
O
N
H
N
2r
1.00
1.08
1.08
1.06
1.08
1.00
3.14
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


170.234
155.255
149.119
136.114
135.700
131.580
125.318
122.021
26.643
14.155
O
N
H
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

2r


8.474
8.158
8.141
7.643
7.627
7.253
7.247
7.240
7.151
7.146
7.141
7.139
7.132
7.089
6.891
6.877
6.865
5.658
2.895
2.885
O
N
H
Ph
1.00
1.03
1.00
1.18
2.23
3.03
2.00
1.06
1.00
1.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

2s


167.604
137.086
135.705
135.190
133.187
132.592
132.114
130.068
128.836
128.375
128.169
128.046
127.436
126.192
125.825
124.861
124.326
26.825
O
N
H
Ph
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)