Supporting Information

Site-Selective Silylation of Aliphatic C–H Bonds Mediated by [1,5]-Hydrogenation Transfer: Synthesis of α-Sila Benzamides

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1. Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.[1] NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, and other commercial suppliers and used as received. Solvents were dried over sodium (for THF and ether) by refluxing for overnight and freshly distilled prior to use. Grignard reagents were purchased from commercial suppliers or prepared by the reaction between related organic halides and magnesium turnings in anhydrous THF, and titrated prior to use.

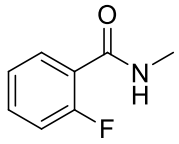
2. Procedure for the Preparation of *N*-Alkyl-Substituted 2-Fluorobenzamides

N-alkyl-substituted 2-fluorobenzamides were prepared by the reaction of related 2-fluorobenzoyl chlorides with alkyl amines. 2-Chloro-*N*-methylbenzamide,[2] 2-bromo-

N-methylbenzamide,[3] 2-iodo-*N*-methylbenzamide[4] were synthesized acoording to the known procedures.

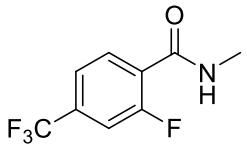
Synthesis of 2-fluorobenzoyl chloride: In a dried flask, 2-fluorobenzoic acid was dissolved in DCM and a few drops of DMF were then added. The resulting solution was added slowly via syringe immersed deeply solution of oxalyl dichloride (3 equiv) in DCM. After stirring at room temperature for 6 h, the volatiles were removed under vacuum. The crude product was used directly for next-step synthesis.

Synthesis of N-alkyl-substituted 2-fluorobenzamide: 2-Fluorobenzoyl chloride, *N*-alkyl-substituted amine (1.5 equiv), Et_3N (2 equiv) and DCM (2 M) were putted into a dried flask and the solution was stirred at room temperature for 3 h. The crude product was then purified by flash chromatography on silica gel to give the product as a white solid or colorless oil (60–96% yields).



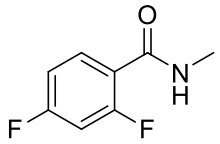
2-Fluoro-*N*-methylbenzamide (1a)

The title compound was obtained as a white solid, Melting point: 48–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–7.96 (m, 1H), 7.40 (d, J = 5.0 Hz, 1H), 7.21–7.17 (m, 1H), 7.08–7.03 (m, 1H), 6.82 (brs, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 160.4 (d, $J_{C\text{-}F}$ = 245 Hz), 132.9 (d, $J_{C\text{-}F}$ = 9.2 Hz), 131.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 124.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.0 (d, $J_{C\text{-}F}$ = 11.8 Hz), 115.8 (d, $J_{C\text{-}F}$ = 25 Hz), 26.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –114.0. IR (neat): 3355, 1646, 1538, 1308, 1308, 1216, 758 cm^{-1}. GC-MS (EI): calcd for C_8H_8FNO [M^+] 153.06, found 153.09. Spectroscopic data are in accordance with those described in the literature.[2]



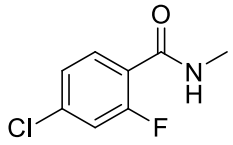
2-Fluoro-*N*-methyl-4-(trifluoromethyl)benzamide (1b)

The title compound was obtained as a white solid. Melting point: 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (t, J = 7.0 Hz, 1H), 7.70 (t, J = 6.8 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 6.79 (brs, 1H), 3.02 (d, J = 4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, $J_{C\text{-}F}$ = 3 Hz), 157.5 (dd, $J_{C\text{-}F}$ = 255, 2.9 Hz), 135.8 (d, $J_{C\text{-}F}$ = 2 Hz), 129.9 (dd, $J_{C\text{-}F}$ = 2 Hz), 124.5 (d, $J_{C\text{-}F}$ = 4 Hz), 122.9 (d, $J_{C\text{-}F}$ = 12 Hz), 122.2 (dd, $J_{C\text{-}F}$ = 271 Hz), 118.9 (dd, $J_{C\text{-}F}$ = 15 Hz), 26.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –61.3, –117.2. IR (neat): 3308, 1659, 1457, 1223, 1079, 776 cm^{-1}. GC-MS (EI): calcd for $C_9H_7F_4NO$ [M^+] 221.05, found 221.08.



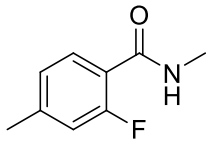
2,4-Difluoro-*N*-methylbenzamide (1c)

The title compound was obtained as a white solid. Melting point: 76–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.07 (m, 1H), 6.96 (t, J = 7.3 Hz, 1H), 6.89–6.77 (m, 1H), 6.69 (brs, 1H), 3.00 (d, J = 3.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6 (dd, $J_{C\text{-}F}$ =254 ,13 Hz), 163.0 (d, $J_{C\text{-}F}$ = 3 Hz), 160.8 (dd, $J_{C\text{-}F}$ =248, 12 Hz), 133.6 (dd, $J_{C\text{-}F}$ = 10.1, 4.0 Hz), 117.5 (dd, $J_{C\text{-}F}$ = 12.1, 3.7 Hz), 112.2 (dd, $J_{C\text{-}F}$ = 21.2, 3.3 Hz), 104.5 (dd, $J_{C\text{-}F}$ = 28, 25 Hz), 26.7; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –104.4 (J = 10.7 Hz), –109.6 (J = 10.7 Hz). IR (neat): 3381, 1645, 1537, 1266, 1076, 765 cm^{-1}. GC-MS (EI): calcd for $C_8H_7F_2NO$ [M^+] 171.05, found 171.08.



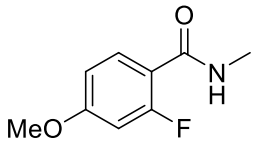
4-Chloro-2-fluoro-*N*-methylbenzamide (1d)

The title compound was obtained as a white solid. Melting point: 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (t, J = 8.4 Hz, 1H), 7.23 (t, J = 9.7 Hz, 1H), 7.12 (d, J = 11.5 Hz, 1H), 6.70 (brs, 1H), 3.00 (d, J = 4.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, $J_{C\text{-}F}$ = 3.4 Hz), 160.1 (d, $J_{C\text{-}F}$ = 249 Hz), 138.3 (d, $J_{C\text{-}F}$ = 11.2 Hz), 132.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 125.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 119.6 (d, $J_{C\text{-}F}$ = 12.1 Hz), 116.6 (d, $J_{C\text{-}F}$ = 29 Hz), 26.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –114.0. IR (neat): 3358, 1644, 1532, 1403, 1078, 901, 769 cm^{-1}. GC-MS (EI): calcd for C_8H_7ClFNO [M$^+$] 187.02, found187.04.



2-Fluoro-*N*,4-dimethylbenzamide (1e)

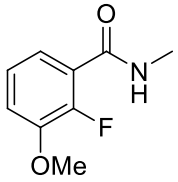
The title compound was obtained as a white solid. Melting point: 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (t, J = 8.2 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H), 6.90 (d, J = 13.2 Hz, 1H), 6.73 (brs, 1H), 3.01 (d, J = 4.5 Hz, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, $J_{C\text{-}F}$ = 3.4 Hz), 160.5 (d, $J_{C\text{-}F}$ = 244 Hz), 144.4 (d, $J_{C\text{-}F}$ = 9.2 Hz), 131.8 (d, $J_{C\text{-}F}$ = 2.8 Hz), 125.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 119.0 (d, $J_{C\text{-}F}$ = 11.7 Hz), 116.3 (d, $J_{C\text{-}F}$ = 25 Hz), 26.7, 21.2 (d, $J_{C\text{-}F}$ = 1.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ = –114.8. IR (neat): 3309, 1634, 1539, 1405, 1065, 730 cm^{-1}. GC-MS (EI): calcd for $C_9H_{10}FNO$ [M$^+$] 167.07, found 167.10.



2-Fluoro-4-methoxy-*N*-methylbenzamide (1f)

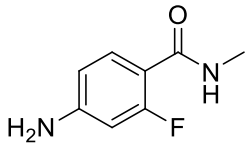
The title compound was obtained as a white solid. Melting point: 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (t, J = 9.1 Hz, 1H), 6.76 (dd, J = 8.8, 2.4 Hz, 1H), 6.67 (brs, 1H), 6.59 (dd, J = 14.1, 2.4 Hz, 1H), 3.82 (s, 3H), 3.04–2.93 (m, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 163.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 163.3 (d, $J_{C\text{-}F}$ = 12.3 Hz), 161.6 (d, $J_{C\text{-}F}$ =245 Hz), 133.6 (d, $J_{C\text{-}F}$ = 4.3 Hz), 113.3 (d, $J_{C\text{-}F}$ = 12.0 Hz), 110.5 (d, $J_{C\text{-}F}$ = 2.5 Hz), 101.4 (d, $J_{C\text{-}F}$ = 29 Hz), 55.7, 26.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –111.3. IR (neat): 3308, 1621, 1439, 1269, 1026, 831, 675 cm^{-1}. GC-MS (EI): calcd for $C_9H_{10}FNO$ [M$^+$] 183.07, found 183.10.



2-Fluoro-3-methoxy-*N*-methylbenzamide (1g)

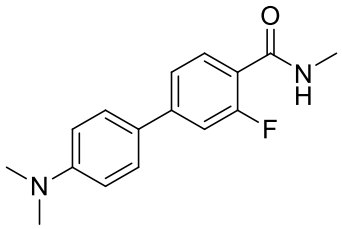
The title compound was obtained as a white solid. Melting point: 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.58 (m, 1H), 7.17–7.13 (m, 1H), 7.10–7.05 (m, 1H), 6.71 (brs, 1H), 3.90 (s, 3H), 3.03 (dd, J = 4.8, 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 150.7 (d, $J_{C\text{-}F}$ = 246 Hz), 147.8 (d, $J_{C\text{-}F}$ = 12.5 Hz), 124.2 (d, $J_{C\text{-}F}$ = 4.4 Hz), 122.4 (d, $J_{C\text{-}F}$ = 1.2 Hz), 122.1 (d, $J_{C\text{-}F}$ = 9.4 Hz), 116.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 56.5, 26.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –111.3. IR (neat): 3292, 1640, 1480, 1270, 1072, 715 cm^{-1}. GC-MS (EI): calcd for $C_9H_{10}FNO$ [M$^+$] 183.07, found 183.10.



4-Amino-2-fluoro-*N*-methylbenzamide (1h)

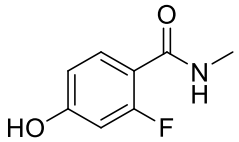
The title compound was obtained as a white solid. Melting point: 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (t, J = 8.6 Hz, 1H), 6.61 (brs, 1H), 6.48 (d, J = 7.8 Hz, 1H), 6.31 (d, J = 14.1 Hz, 1H), 4.11 (brs, 2H), 2.98 (d, J = 3.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 162.2 (d, $J_{C\text{-}F}$ = 243Hz), 151.3 (d, $J_{C\text{-}F}$ = 12.7 Hz), 133.3 (d, $J_{C\text{-}F}$ = 4.4 Hz), 110.9 (d, $J_{C\text{-}F}$ = 1.8 Hz), 110.4 (d, $J_{C\text{-}F}$ = 12 Hz), 100.8 (d, $J_{C\text{-}F}$

= 29 Hz), 26.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –112.9. IR (neat): 3674, 2987, 1632, 1406, 1250, 1065, 891 cm^{-1}. GC-MS (EI): calcd for $C_8H_9FN_2O$ [M$^+$] 168.07, found 168.09.



4'-(Dimethylamino)-3-fluoro-*N*-methyl-[1,1'-biphenyl]-4-carboxamide (1i)

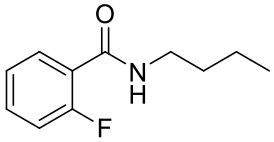
The title compound was obtained as a white solid. Melting point: 153–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (t, J = 8.4 Hz, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 9.4 Hz, 1H), 7.20 (d, J = 13.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 3H), 2.96 (d, J = 4.6 Hz, 3H), 2.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1 (d, $J_{C\text{-}F}$ = 3.4 Hz), 161.1 (d, $J_{C\text{-}F}$ = 244 Hz), 150.7, 146.5 (d, $J_{C\text{-}F}$ = 9.3 Hz), 132.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.7, 126.9, 125.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 121.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 117.7 (d, $J_{C\text{-}F}$ = 11.9 Hz), 113.0, 112.6 (d, $J_{C\text{-}F}$ = 26 Hz), 112.5, 40.3, 26.7; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.9. IR (neat): 3299, 1636, 1557, 1403, 1076, 808, 773 cm^{-1}. GC-MS (EI): calcd for $C_{16}H_{17}FN_2O$ [M$^+$] 272.13, found 272.09.



2-Fluoro-4-hydroxy-*N*-methylbenzamide (1j)

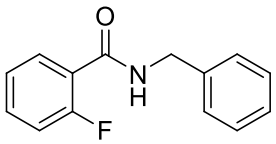
The title compound was obtained as a white solid. Melting point: 104–106 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.44 (s, 1H), 7.93 (s, 1H), 7.60 (t, J = 8.8 Hz, 1H), 6.71 (d, J = 9.4 Hz, 1H), 6.64 (d, J = 13.0 Hz, 1H), 2.80 (d, J = 4.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.2 (d, $J_{C\text{-}F}$ = 2.3 Hz), 161.5 (d, $J_{C\text{-}F}$ = 12 Hz), 161.0 (d, $J_{C\text{-}F}$ = 247 Hz), 132.1 (d, $J_{C\text{-}F}$ = 4.9 Hz), 114.4 (d, $J_{C\text{-}F}$ = 13.6 Hz), 112.1 (d, $J_{C\text{-}F}$ = 2.5 Hz), 103.1 (d, $J_{C\text{-}F}$ = 25 Hz), 26.8; ^{19}F NMR (377 MHz, DMSO-d_6): δ = –111.6. IR

(neat): 3480, 1615, 1548, 1252, 1089, 850, 756 cm^{-1}. GC-MS (EI): calcd for $C_8H_8FNO_2$ [M^+] 169.05, found 169.07.



***N*-butyl-2-fluorobenzamide (1k)**

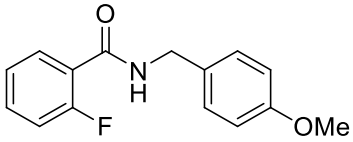
The title compound was obtained as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (t, J = 7.8 Hz, 1H), 7.38 (dd, J = 13.4, 7.1 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.03 (dd, J = 11.6, 8.7 Hz, 1H), 6.75 (brs, 1H), 3.42 (dd, J = 13.0, 6.6 Hz, 2H), 1.60–1.51 (m, 2H), 1.41–1.31 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 161.4 (d, $J_{C\text{-}F}$ = 245 Hz), 132.8 (d, $J_{C\text{-}F}$ = 9.3 Hz), 131.75 (d, $J_{C\text{-}F}$ = 2.2 Hz), 124.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 121.3 (d, $J_{C\text{-}F}$ = 11.8 Hz), 115.7 (d, $J_{C\text{-}F}$ = 25 Hz), 39.6, 31.4, 20.0, 13.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –114.1. IR (neat): 3307, 1644, 1532, 1481, 1305, 754 cm^{-1}. GC-MS (EI): calcd for $C_{11}H_{14}FNO$ [M^+] 195.11, found 195.12. Spectroscopic data are in accordance with those described in the literature.[5]



***N*-benzyl-2-fluorobenzamide (1l)**

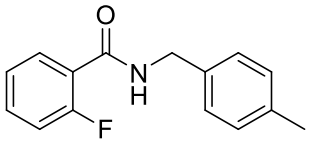
The title compound was obtained as a white solid. Melting point: 67–69 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (t, J = 7.7 Hz, 1H), 7.46 (dd, J = 13.2, 6.4 Hz, 1H), 7.35 (t, J = 6.1 Hz, 4H), 7.31–7.24 (m, 2H), 7.10 (dd, J = 12.0, 8.4 Hz, 2H), 4.68 (d, J = 5.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 160.6 (d, $J_{C\text{-}F}$ = 245 Hz), 138.0, 133.3 (d, $J_{C\text{-}F}$ = 9.3 Hz), 132.1 (d, $J_{C\text{-}F}$ = 2.0 Hz), 128.7, 127.7, 127.5, 124.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 120.9 (d, $J_{C\text{-}F}$ = 11.5 Hz), 116.0 (d, $J_{C\text{-}F}$ = 25 Hz), 44.0; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.5. IR (neat): 3262, 1637, 1538, 1225, 1078,

779, 731 cm^{-1}. GC-MS (EI): calcd for $C_{14}H_{12}FNO$ [M^+] 229.09, found 229.13. Spectroscopic data are in accordance with those described in the literature.[6]



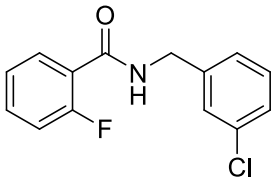
2-Fluoro-*N*-(4-methoxybenzyl)benzamide (1m)

The title compound was obtained as a white solid. Melting point: 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 12.8, 6.1 Hz, 1H), 7.27 (dd, J = 15.5, 7.6 Hz, 3H), 7.09 (dd, J = 11.8, 8.5 Hz, 1H), 6.99 (s, 1H), 6.88 (d, J = 8.3 Hz, 2H), 4.61 (d, J = 5.1 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 160.6 (d, $J_{C\text{-}F}$ = 256 Hz), 159.0, 133.3 (d, $J_{C\text{-}F}$ = 9.4 Hz), 132.1, 130.0, 129.1, 124.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 122.0 (d, $J_{C\text{-}F}$ = 11.5 Hz), 116.0 (d, $J_{C\text{-}F}$ = 11.5 Hz), 114.1, 55.3, 43.5; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.5. IR (neat): 3302, 1639, 1511, 1250, 1214, 1034, 754 cm^{-1}. GC-MS (EI): calcd for $C_{15}H_{14}FNO_2$ [M^+] 259.10, found 259.11.



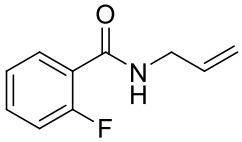
2-Fluoro-*N*-(4-methylbenzyl)benzamide (1n)

The title compound was obtained as a white solid. Melting point: 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (t, J = 7.6 Hz, 1H), 7.44 (dd, J = 12.7, 6.1 Hz, 1H), 7.25 (d, J = 7.3 Hz, 3H), 7.15 (d, J = 7.6 Hz, 2H), 7.08 (dd, J = 11.9, 8.5 Hz, 2H), 4.63 (d, J = 5.1 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 160.5 (d, $J_{C\text{-}F}$ = 245 Hz), 137.1, 134.9, 133.2 (d, $J_{C\text{-}F}$ = 9.3 Hz), 132.0 (d, $J_{C\text{-}F}$ = 1.7 Hz), 129.3, 127.7, 124.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 122.0 (d, $J_{C\text{-}F}$ = 11.5 Hz), 115.9 (d, $J_{C\text{-}F}$ = 24 Hz), 43.8, 21.0; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.4. IR (neat):3278, 1639, 1531, 1406, 1065, 780 cm^{-1}. GC-MS (EI): calcd for $C_{15}H_{14}FNO$ [M^+] 243.11, found 243.13.



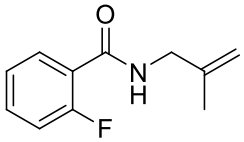
***N*-(3-chlorobenzyl)-2-fluorobenzamide (1o)**

The title compound was obtained as a white solid. Melting point: 88–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–8.02 (m, 1H), 7.44–7.36 (m, 1H), 7.23–7.14 (m, 4H), 7.10–6.98 (m, 2H), 4.58 (d, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 160.6 (d, $J_{C\text{-}F}$ = 246 Hz), 140.1, 134.5, 133.5 (d, $J_{C\text{-}F}$ = 9.4 Hz), 132.2 (d, $J_{C\text{-}F}$ = 2.0 Hz), 123.0, 127.7 (d, $J_{C\text{-}F}$ = 4.0 Hz), 125.8, 124.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 120.6 (d, $J_{C\text{-}F}$ = 11.4 Hz), 116.0 (d, $J_{C\text{-}F}$ = 25 Hz), 115.6(d, $J_{C\text{-}F}$ = 21 Hz), 43.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.3. IR (neat): 3310, 1663, 1551, 1224, 1054, 765, 680 cm^{-1}. GC-MS (EI): calcd for $C_{14}H_{11}ClFNO$ [M^+] 263.05, found 263.07.



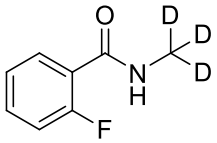
***N*-Allyl-2-fluorobenzamide (1p)**

The title compound was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.0 (m, 1H), 7.42–7.36 (m, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.04 (dd, J = 12.1, 8.3 Hz, 1H), 6.78 (brs, 1H), 5.92–5.82 (m, 1H), 5.20 (dd, J = 17.2, 1.3 Hz, 1H), 5.11 (dd, J = 10.3, 1.2 Hz, 1H), 4.06–4.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 160.6 (d, $J_{C\text{-}F}$ = 245 Hz), 133.8, 133.2 (d, $J_{C\text{-}F}$ = 9.3 Hz), 132.0 (d, $J_{C\text{-}F}$ = 1.3 Hz), 124.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 120.9 (d, $J_{C\text{-}F}$ = 11.6 Hz), 116.4, 115.9 (d, $J_{C\text{-}F}$ = 11.6 Hz), 42.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.7. IR (neat): 3306, 1651, 1532, 1482, 1303, 1098, 895, 785 cm^{-1}. GC-MS (EI): calcd for $C_{10}H_{10}FNO$ [M^+] 179.07, found 179.10.



2-Fluoro-*N*-(2-methylallyl)benzamide (1q)

The title compound was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.98 (m, 1H), 7.43–7.37 (m, 1H), 7.23–7.14 (m, 1H), 7.08–7.03 (m, 1H), 6.89 (brs, 1H), 4.84 (dd, J = 10.1, 8.8 Hz, 2H), 3.98 (d, J = 5.8 Hz, 2H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 160.4 (d, $J_{C\text{-}F}$ = 246 Hz), 141.5, 133.0 ($J_{C\text{-}F}$ = 9.3 Hz), 131.8, 124.6 ($J_{C\text{-}F}$ = 3.1 Hz), 121.0 ($J_{C\text{-}F}$ = 11.7 Hz), 115.8 ($J_{C\text{-}F}$ = 25 Hz),, 110.8, 45.2, 20.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.8. IR (neat): 3326, 1632, 1501, 1493, 1357, 1172, 932, 756 cm^{-1}. GC-MS (EI): calcd for $C_{11}H_{12}FNO$ [M$^+$] 193.09, found 193.12.

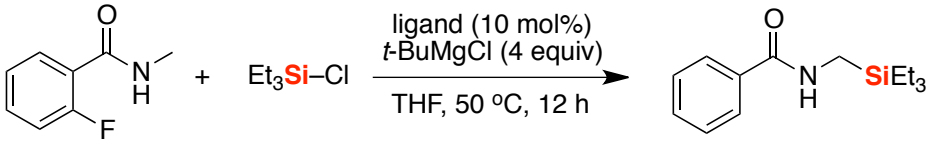


1a-*d*$_3$

The title compound was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.08 (m, 1H), 7.49–7.43 (m, 1H), 7.28–7.23 (m, 1H), 7.11 (dd, J = 12.1, 8.3 Hz, 1H), 6.77 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 160.6 (d, $J_{C\text{-}F}$ = 245 Hz), 133.1 (d, $J_{C\text{-}F}$ = 9.3 Hz), 132.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 124.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 122.0 (d, $J_{C\text{-}F}$ = 11.7 Hz), 115.9 (d, $J_{C\text{-}F}$ = 24 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ = –114.0. IR (neat): 3359, 1632, 1575, 1325, 1245, 760 cm^{-1}. GC-MS (EI): calcd for $C_8H_5D_3FNO$ [M$^+$] 156.08, found 156.10.

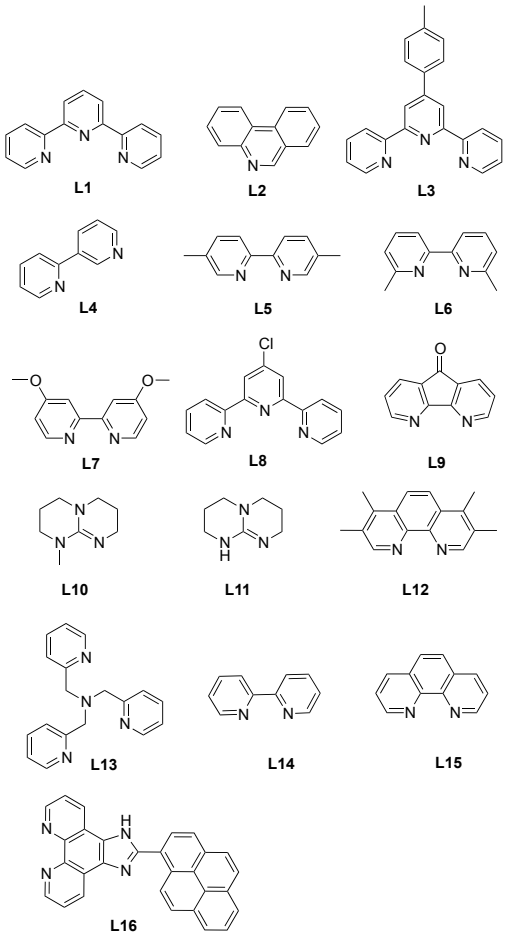
3. Optimizing Reaction Parameters

Table S1. Investigation of the Effect of Ligands on the Silylation[a]



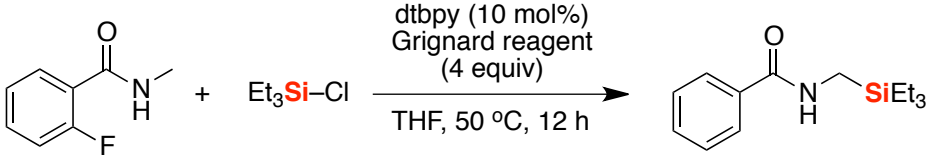
1a **2a** **3aa**

Entry	Ligand	Yield (%)[b]
1	--	12
2	dtbpy	76
3	**L1**	39
4	**L2**	20
5	**L3**	23
6	**L4**	13
7	**L5**	38
8	**L6**	37
9	**L7**	44
10	**L8**	42
11	**L9**	31
12	**L10**	<10
13	**L11**	<10
14	**L12**	26
15	**L13**	18
16	**L14**	32
17	**L15**	16
18	**L16**	16
19	TMEDA	13



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (4 equiv), Ligand (10 mol%), *t*-BuMgCl (4 equiv), in THF (0.5 mL), 50 °C, 12 h. [b]Isolated yield.

Table S2. Investigation of the Effect of Grignard Reagents on the Silylation[a]



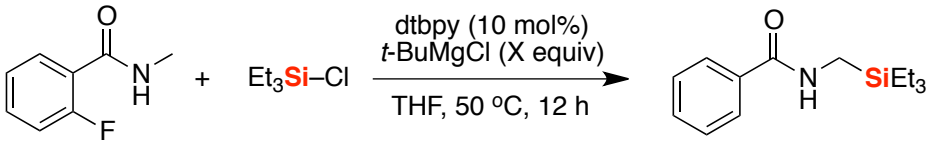
1a **2a** **3aa**

Entry	Grignard Reagent	Yield (%)[b]
1	PhMgBr	nd
2	$TMSCH_2MgCl$	nd

3	BnMgCl	nd
4	MeMgBr	nd
5	AllylMgBr	nd
6	VinylMgBr	18
7	CyMgCl	28
8	EtMgBr	14
9	*i*-PrMgCl	20
10	*t*-BuMgCl	76
11	*n*-HepMgBr	12
12	*i*-PrMgCl•LiCl	20

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (4 equiv), dtbpy (10 mol%), Grignard reagent (4 equiv), THF (0.5 mL), 50 °C, 12 h. [b]Isolated yield.

Table S3. Investigating the Effect of the Amount of *t*-BuMgCl on the Silylation[a]

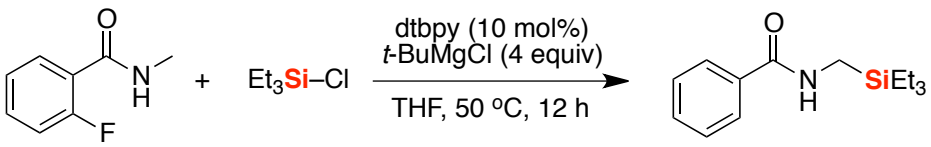


1a **2a** **3aa**

Entry	Ligand	Grignard Reagent	Yield (%)[b]
1	dtbpy	*t*-BuMgCl (0.2 equiv)	nd
2	dtbpy	*t*-BuMgCl (0.5 equiv)	nd
3	dtbpy	*t*-BuMgCl (1.0 equiv)	nd
4	dtbpy	*t*-BuMgCl (2.0 equiv)	24
5	dtbpy	*t*-BuMgCl(2.5 equiv)	37
6	dtbpy	*t*-BuMgCl(3.0 equiv)	49
7	dtbpy	*t*-BuMgCl(3.5 equiv)	51
8	dtbpy	*t*-BuMgCl(4.0 equiv)	76
9	dtbpy	*t*-BuMgCl(5.0 equiv)	67
10	dtbpy	*t*-BuMgCl(6.0 equiv)	65

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (4 equiv), dtbpy (10 mol%), *t*-BuMgCl, THF (0.5 mL), 50 °C, 12 h. [b]Isolated yield.

Table S4. Investigating the Effect of the Amount of Chlorotriethylsilane[a]



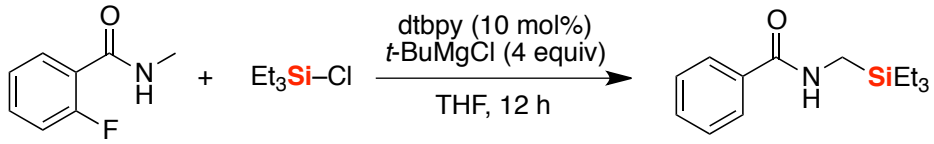
1a **2a** **3aa**

Entry	Ligand	Et_3Si–Cl	Grignard Reagent	Yield (%)[b]

1	dtbpy	2 equiv	*t*-BuMgCl (4 equiv)	48
2	dtbpy	3 equiv	*t*-BuMgCl (4 equiv)	58
3	dtbpy	4 equiv	*t*-BuMgCl (4 equiv)	76
4	dtbpy	5 equiv	*t*-BuMgCl (4 equiv)	56
5	dtbpy	6 equiv	*t*-BuMgCl (4 equiv)	47

[a]Reaction conditions: **1a** (0.2 mmol), **2a**, dtbpy (10 mol%), *t*-BuMgCl (4 equiv), THF (0.5 mL), 50 °C, 12 h. [b]Isolated yield.

Table S5. Investigation of the Effect of Temperature on the Silylation[a]

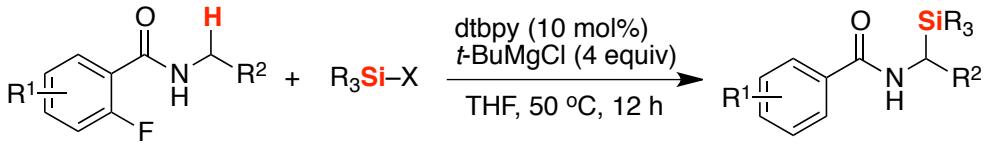


1a **2a** **3aa**

Entry	Ligand	T (°C)	Grignard	Yield(%)[b]
1	dtbpy	25	*t*-BuMgCl(4 equiv)	42
2	dtbpy	30	*t*-BuMgCl(4 equiv)	43
3	dtbpy	40	*t*-BuMgCl(4 equiv)	50
4	dtbpy	50	*t*-BuMgCl(4 equiv)	76
5	dtbpy	60	*t*-BuMgCl(4 equiv)	36
6	dtbpy	70	*t*-BuMgCl(4 equiv)	35

[a]Reaction conditions: **1a** (0.2 mmol), **2a**, dtbpy (10 mol%), *t*-BuMgCl (4 equiv), THF (0.5 mL), 12 h. [b]Isolated yield.

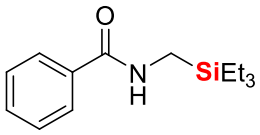
4. General Procedure for the Silylation of α-C(sp^3)–H Bonds



1 **2** **3**

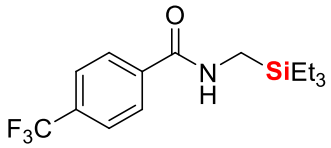
In a dried Schlenk tube were placed 2-fluorobenzamides **1** (0.2 mmol), silane **2** (0.8 mmol) and dtbpy (6 mg, 0.02 mmol), then a freshly distilled THF (0.5–0.6 mL) was added by a syringe under nitrogen atmosphere. *tert*-Butylmagnesium chloride (0.8–1.2 mL, 1.0 M in THF, 0.8 mmol or 1.2 mmol) was dropwise added at 50 °C and the

mixture was stirred for 12 h. After quenched by a solution of NH_4Cl, the crude product was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was further purified by flash chromatography on silica gel to afford the desired α-sila benzamide **3**.



***N*-[(triethylsilyl)methyl]benzamide (3aa)**

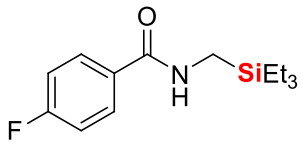
The general procedure was applied to 2-fluoro-*N*-methylbenzamide (31 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (38 mg, 76% yield). Melting point: 44–46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 6.29 (brs, 1H), 2.97 (d, J = 5.7 Hz, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.61 (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 135.0, 130.9, 128.3, 126.6, 26.0, 7.1, 2.5. IR (neat): 3302, 1630, 1542, 1312, 1015, 883, 744 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{14}H_{22}NOSi$ $[M-H]^-$ 248.1471, found 248.1464.



***N*-[(triethylsilyl)methyl]-4-(trifluoromethyl)benzamide (3ab)**

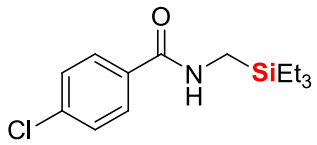
The general procedure was applied to 2-fluoro-*N*-methyl-4-(trifluoromethyl)benzamide (45 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8

mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (53 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 6.17 (brs, 1H), 3.02 (d, J = 5.7 Hz, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 135.9, 131.1 (d, $J_{C\text{-}F}$ = 22 Hz), 129.8, 129.1, 123.9 (d, $J_{C\text{-}F}$ = 22 Hz), 123.7 (d, $J_{C\text{-}F}$ = 271 Hz), 26.4, 7.2, 2.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –62.8. IR (neat): 3279, 1633, 1548, 1305, 1127, 797, 696 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{15}H_{21}F_3NOSi$ [M-H]$^-$ 316.1345, found 316.1329.



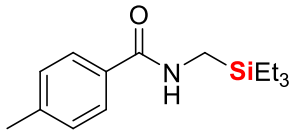
4-Fluoro-*N*-[(triethylsilyl)methyl]benzamide (3ac)

The general procedure was applied to 2,4-difluoro-*N*-methylbenzamide (35 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (37 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (dd, J = 8.0, 5.6 Hz, 2H), 7.08 (t, J = 8.5 Hz, 2H), 5.89 (brs, 1H), 3.00 (d, J = 5.6 Hz, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 164.5 (d, $J_{C\text{-}F}$ = 250 Hz), 131.3 (d, $J_{C\text{-}F}$ = 4 Hz), 128.9 (d, $J_{C\text{-}F}$ = 9 Hz), 115.5 (d, $J_{C\text{-}F}$ = 22 Hz), 26.1, 7.3, 2.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –108.8. IR (neat): 3296, 1632, 1504, 1235, 849, 744 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{14}H_{21}FNOSi$ [M-H]$^-$ 266.1376, found 266.1365.



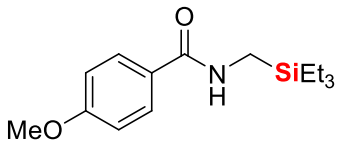
4-Chloro-*N*-[(triethylsilyl)methyl]benzamide (3ad)

The general procedure was applied to 4-chloro-2-fluoro-*N*-methylbenzamide (38 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (1.2 mL, 1.0 M in THF, 1.2 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (29 mg, 51% yield). Melting point: 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 5.93 (brs, 1H), 3.00 (d, J = 5.7 Hz, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 137.3, 133.5, 128.8, 128.1, 26.2, 7.3, 2.6. IR (neat): 3296, 1629, 1585, 1318, 1248, 1017, 823, 741 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{14}H_{21}ClNOSi$ [M+Cl]$^-$ 318.0848, found 318.0836.



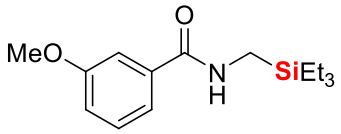
4-Methyl-*N*-[(triethylsilyl)methyl]benzamide (3ae)

The general procedure was applied to 2-fluoro-*N*,4-dimethylbenzamide (34 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (29 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.93 (brs, 1H), 3.00 (d, J = 5.6 Hz, 2H), 2.38 (s, 3H), 0.99 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 141.4, 132.3, 129.2, 126.6, 25.9, 21.4, 7.3, 2.6. IR (neat): 3304, 1628, 1547, 1322, 1016, 743 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{15}H_{24}NOSi$ [M-H]$^-$ 262.1627, found 262.1615.



4-Methoxy-*N*-[(triethylsilyl)methyl]benzamide (3af)

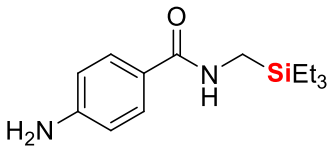
The general procedure was applied to 2-fluoro-4-methoxy-*N*-methylbenzamide (37 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (27 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 5.83 (brs, 1H), 3.84 (s, 3H), 3.00 (d, J = 5.6 Hz, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 161.9, 128.4, 127.5, 113.8, 55.4, 25.9, 7.3, 2.6. IR (neat): 3304, 1624, 1505, 1254, 1035, 843, 743 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{15}H_{24}NO_2Si$ $[M-H]^-$ 278.1576, found 278.1563.



3-Methoxy-*N*-[(triethylsilyl)methyl]benzamide (3ag)

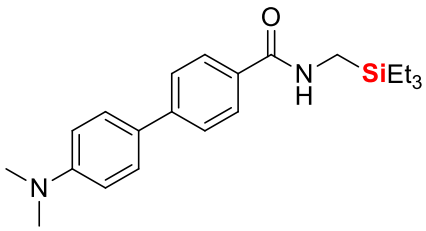
The general procedure was applied to 2-fluoro-5-methoxy-*N*-methylbenzamide (37 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (30 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 2H), 7.20 (d, J = 7.7 Hz, 1H), 7.01 – 6.99 (m, 1H), 5.98 (brs, 1H), 3.83 (s, 3H), 3.00 (d, J = 5.7 Hz, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 159.8, 136.6, 129.5, 118.3, 117.2, 112.2, 55.3, 26.0, 7.3, 2.5. IR (neat): 3296, 1629, 1543, 1249,

1017, 823, 741 cm^{-1}. HRMS ($APCI^+$): calcd for $C_{15}H_{26}NO_2Si$ $[M+H]^+$ 280.1733, found 280.1715.



4-Amino-*N*-[(triethylsilyl)methyl]benzamide (3ah)

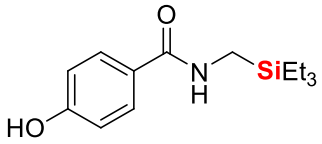
The general procedure was applied to 4-amino-2-fluoro-*N*-methylbenzamide (34 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a colorless oil (32 mg, 60% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 5.75 (brs, 1H), 3.96 (brs, 2H), 2.98 (d, J = 5.6 Hz, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 149.2, 128.3, 124.8, 114.2, 25.7, 7.3, 2.6. IR (neat): 3337, 1605, 1505, 1296, 1016, 744 cm^{-1}. HRMS ($APCI^-$): calcd for $C_{14}H_{23}N_2OSi$ $[M-H]^-$ 263.1580, found 263.1579.



4'-(Dimethylamino)-*N*-[(triethylsilyl)methyl]-[1, 1'-biphenyl]-4-carboxamide (3ai)

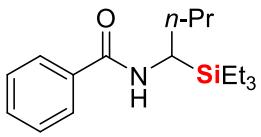
The general procedure was applied to 4'-(dimethylamino)-3-fluoro-*N*-methyl-[1,1'-biphenyl]-4-carboxamide (55 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a white solid (74 mg, 63% yield). Melting point: 107–109 °C. ^1H NMR (400 MHz,

$CDCl_3$): δ = 7.74 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.95 (brs, 1H), 3.04 (d, J = 5.6 Hz, 2H), 3.01 (s, 6H), 1.02 (t, J = 7.9 Hz, 9H), 0.66 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 150.4, 144.0, 132.3, 127.7, 127.69, 127.1, 126.1, 112.6, 40.4, 26.0, 7.3, 2.6. IR (neat): 3290, 1605, 1538, 1218, 1006, 812, 719 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{22}H_{33}N_2OSi$ $[M+H]^+$ 369.2362, found 369.2361.



4-Hydroxy-*N*-[(triethylsilyl)methyl]benzamide (3aj)

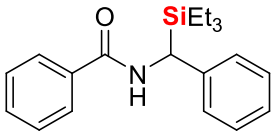
The general procedure was applied to 2-fluoro-4-hydroxy-*N*-methylbenzamide (34 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (1.2 mL, 1.0 M in THF, 1.2 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound as a white solid (22 mg, 40% yield). Melting point: 69–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (brs, 1H), 7.55 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.00 (brs, 1H), 3.01 (d, J = 5.7 Hz, 2H), 0.98 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 160.1, 128.5, 125.7, 115.7, 26.2, 7.3, 2.6. IR (neat): 3152, 1607, 1504, 1278, 1010, 846, 741 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{14}H_{24}NO_2Si$ $[M+H]^+$ 266.1576, found 266.1573.



***N*-[1-(triethylsilyl)butyl]benzamide (3ak)**

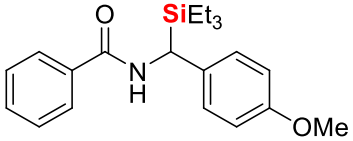
The general procedure was applied to *N*-butyl-2-fluorobenzamide (40 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/20) to

afford the title compound as a white solid (14 mg, 23% yield). Melting point: 172–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 6.9 Hz, 2H), 7.50–7.46 (m, 1H), 7.42 (t, J = 7.2 Hz, 2H), 5.76 (d, J = 9.8 Hz, 1H), 3.99–3.93 (m, 1H), 1.60–1.36 (m, 4H), 1.01 (t, J = 8.0 Hz, 9H), 0.91 (t, J = 7.1 Hz, 3H), 0.63 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 135.4, 131.0, 128.6, 126.6, 38.3, 34.1, 20.6, 13.9, 7.6, 2.2. IR (neat): 3282, 1626, 1537, 1328, 1016, 711 cm^{-1}. HRMS (APCI^{+}): calcd for $C_{17}H_{30}NOSi$ $[M+H]^{+}$ 292.2097, found 292.2095.



***N*-[phenyl(triethylsilyl)methyl]benzamide (3al)**

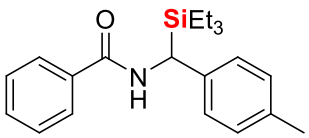
The general procedure was applied to *N*-benzyl-2-fluorobenzamide (46 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (1.2 mL, 1.0 M in THF, 1.2 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (27 mg, 40% yield). Melting point: 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 7.0 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 7.24–7.19 (m, 2H), 7.12–7.06 (m, 3H), 6.53 (d, J = 8.5 Hz, 1H), 4.91 (d, J = 8.8 Hz, 1H), 0.89 (t, J = 7.9 Hz, 9H), 0.57 (q, J = 7.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 141.7, 135.0, 131.4, 128.7, 128.4, 126.8, 125.9, 125.7, 44.4, 7.4, 2.0. IR (neat): 3293, 1628, 1537, 1313, 1007, 704 cm^{-1}. HRMS (APCI^{+}): calcd for $C_{20}H_{28}NOSi$ $[M+H]^{+}$ 326.1940, found 326.1939.



***N*-[(4-methoxyphenyl)(triethylsilyl)methyl]benzamide (3am)**

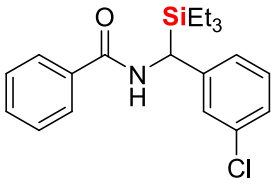
The general procedure was applied to 2-fluoro-*N*-(4-methoxybenzyl)benzamide (52 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium

chloride (1.2 mL, 1.0 M in THF, 1.2 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (24 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.55 (d, J = 8.7 Hz, 1H), 4.92 (d, J = 8.8 Hz, 1H), 3.77 (s, 3H), 0.97 (d, J = 8.0 Hz, 8H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 157.7, 135.1, 133.8, 131.3, 128.6, 127.2, 126.8, 114.0, 55.2, 43.8, 7.4, 2.1. IR (neat): 3301, 1630, 1509, 1245, 1035, 830, 714 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{21}H_{28}NO_2Si$ [M-H]$^-$ 354.1889, found 354.1892.



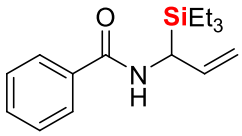
***N*-[p-tolyl(triethylsilyl)methyl]benzamide (3an)**

The general procedure was applied to 2-fluoro-*N*-(4-methylbenzyl)benzamide (49 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (1.2 mL, 1.0 M in THF, 1.2 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (28 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.4 Hz, 2H), 7.53–7.47 (m, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.13–7.01 (m, 4H), 6.56 (d, J = 8.5 Hz, 1H), 4.94 (d, J = 8.8 Hz, 1H), 2.30 (s, 3H), 0.96 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 138.5, 135.2, 135.1, 131.3, 129.1, 128.6, 126.8, 125.9, 44.2, 21.0, 7.4, 2.1. IR (neat): 3298, 1630, 1512, 1312, 1019, 819, 713 cm^{-1}. HRMS (APCI$^-$): calcd for $C_{21}H_{28}NOSi$ [M-H]$^-$ 338.1940, found 338.1930.



***N*-[(3-chlorophenyl)(triethylsilyl)methyl]benzamide (3ao)**

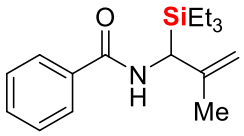
The general procedure was applied to *N*-(3-chlorobenzyl)-2-fluorobenzamide (53 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (1.2 mL, 1.0 M in THF, 1.2 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (28 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (t, J = 7.8 Hz, 1H), 7.50 (d, J = 7.0 Hz, 1H), 7.37–7.05 (m, 8H), 4.93 (d, J = 7.4 Hz, 1H), 0.96 (t, J = 7.8 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 144.1, 134.4, 133.4, 132.4, 129.6, 125.8, 125.0, 124.0, 116.1, 115.9, 44.2, 7.2, 1.8. IR (neat): 3312, 1651, 1521, 1479, 1293, 1097, 786, 755 cm^{-1}. HRMS (APCI^{+}): calcd for $C_{20}H_{26}ClNOSi$ $[M+Na]^{+}$ 382.1370, found 382.1351.



***N*-[1-(triethylsilyl)allyl]benzamide (3ap)**

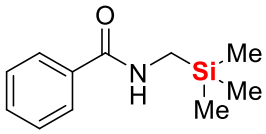
The general procedure was applied to *N*-allyl-2-fluorobenzamide (90 mg, 0.5 mmol), triethylchlorosilane (303 mg, 2.0 mmol), *tert*-butylmagnesium chloride (2.0 mL, 1.0 M in THF, 2.0 mmol) and dtbpy (15 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (69 mg, 50% yield). Melting point: 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 6.12 (d, J = 8.6 Hz, 1H), 6.00–5.92 (m, 1H), 5.03–4.99 (m, 1H), 4.98 (d, J = 1.7 Hz, 1H), 4.64–4.52 (m, 1H), 1.02 (t, J = 7.9 Hz, 9H), 0.68 (q,

J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 136.6, 135.0, 131.3, 128.7, 126.7, 110.3, 42.7, 7.4, 2.0. IR (neat): 3278, 1626, 1532, 1324, 1010, 714 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{16}H_{26}NOSi$ $[M+H]^+$ 276.1784, found 276.1780. Spectroscopic data are in accordance with those described in the literature.[7]



***N*-[2-methyl-1-(triethylsilyl)allyl]benzamide (3aq)**

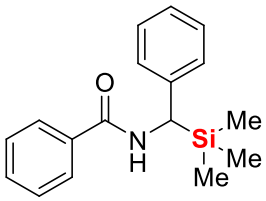
The general procedure was applied to 2-fluoro-*N*-(2-methylallyl)benzamide (97 mg, 0.5 mmol), triethylchlorosilane (303 mg, 2.0 mmol), *tert*-butylmagnesium chloride (2.0 mL, 1.0 M in THF, 2.0 mmol) and dtbpy (15 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a colorless oil (56 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 6.9 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 6.28 (d, J = 8.6 Hz, 1H), 4.79 (s, 1H), 4.73 (s, 1H), 4.41 (d, J = 9.1 Hz, 1H), 1.82 (s, 3H), 1.02 (t, J = 7.9 Hz, 9H), 0.70 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 145.0, 135.1, 131.3, 128.6, 126.7, 108.4, 45.5, 22.0, 7.5, 2.5. IR (neat): 3310, 1644, 1515, 1280, 1073, 710 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{17}H_{27}NOSiCl$ $[M+Cl]^-$ 324.1550, found 324.1551.



***N*-[(trimethylsilyl)methyl]benzamide (3ba)**

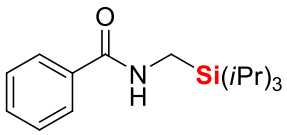
The general procedure was applied to 2-fluoro-*N*-methylbenzamide (31 mg, 0.2 mmol), trimethylsilyl cyanide (80 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 ºC for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (26 mg, 62% yield). Melting point:

113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.4 Hz, 2H), 6.29 (brs, 1H), 2.92 (d, J = 5.8 Hz, 2H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 135.1, 131.0, 128.4, 126.7, 30.3, -2.6. IR (neat): 3300, 1625, 1548, 1325, 1247, 833, 694 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{11}H_{18}NOSi$ $[M+H]^+$ 208.1158, found 208.1151.



_N_-[phenyl(trimethylsilyl)methyl]benzamide (3ca)

The general procedure was applied to *N*-benzyl-2-fluorobenzamide (46 mg, 0.2 mmol), chlorotrimethylsilane (87 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (20 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 7.1 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.31–7.26 (m, 2H), 7.16 (t, J = 7.3 Hz, 3H), 6.55 (d, J = 7.1 Hz, 1H), 4.83 (d, J = 8.7 Hz, 1H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 141.3, 135.1, 131.4, 128.6, 128.4, 126.8, 125.9, 125.8, 46.9, –3.2. IR (neat): 3302, 1631, 1532, 1249, 842, 700 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{17}H_{22}NOSi$ $[M+H]^+$ 284.1471, found 284.1468.



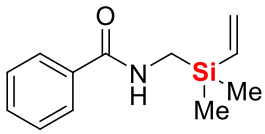
_N_-[(triisopropylsilyl)methyl]benzamide (3da)

The general procedure was applied to 2-fluoro-*N*-methylbenzamide (31 mg, 0.2 mmol), triisopropylsilyl chloride (155 mg, 0.8 mmol), *tert*-butylmagnesium chloride

(0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (16 mg, 27% yield). Melting point: 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 6.9 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 5.92 (brs, 1H), 3.12 (d, J = 5.5 Hz, 2H), 1.18–1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 135.2, 131.2, 128.6, 126.6, 23.8, 18.6, 10.5. IR (neat): 3286, 1646, 1541, 1320, 1074, 884, 714 cm^{-1}. HRMS (APCI^{+}): calcd for $C_{17}H_{30}NOSi$ $[M+H]^{+}$ 292.2097, found 292.2095.

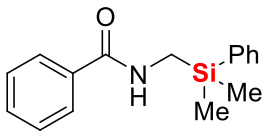
***N*-[(tert-butyldimethylsilyl)methyl]benzamide (3ea)**

The general procedure was applied to 2-fluoro-*N*-methylbenzamide (31 mg, 0.2 mmol), *tert*-butyldimethylsilyl trifluoromethanesulfonate (212 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (15 mg, 30% yield). Melting point: 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 6.9 Hz, 2H), 7.48 (t, J = 6.6 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 5.91 (brs, 1H), 3.02 (d, J = 5.7 Hz, 2H), 0.95 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 135.2, 131.2, 128.6, 126.7, 27.0, 26.5, 16.5, -6.9. IR (neat): 3234, 1626, 1553, 1397, 1229, 895, 702 cm^{-1}. HRMS (APCI^{+}): calcd for $C_{14}H_{24}NOSi$ $[M+H]^{+}$ 250.1627, found 250.1619.



***N*-[(dimethyl(vinyl)silyl)methyl]benzamide (3fa)**

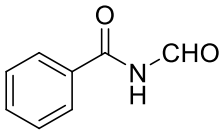
The general procedure was applied to 2-fluoro-*N*-methylbenzamide (31 mg, 0.2 mmol), chlorodimethyl(vinyl)silane (97 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (6 mg, 13% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.0 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 6.24–6.07 (m, 2H), 5.92 (brs, 1H), 5.82 (dd, J = 19.7, 4.3 Hz, 1H), 3.01 (d, J = 5.7 Hz, 2H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 136.5, 135.1, 134.0, 131.2, 128.6, 126.7, 28.9, –4.4. IR (neat): 3303, 1633, 1544, 1312, 893, 838, 698 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{12}H_{18}NOSi$ $[M+H]^+$ 220.1158, found 220.1144.



***N*-[(dimethyl(phenyl)silyl)methyl]benzamide (3ga)**

The general procedure was applied to 2-fluoro-*N*-methylbenzamide (78 mg, 0.5 mmol), chlorodimethyl(phenyl)silane (342 mg, 2.0 mmol), *tert*-butylmagnesium chloride (2.0 mL, 1.0 M in THF, 2.0 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (68 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.55 (m, 4H), 7.44–7.34 (m, 6H), 5.88 (brs, 1H), 3.17 (d, J = 5.7 Hz, 2H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 136.4, 134.9, 133.7, 131.1, 129.7, 128.5, 128.2, 126.6, 29.3, –4.1. IR (neat): 3303, 1632, 1541, 1312, 1113, 836, 698 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{16}H_{20}NOSi$ $[M+H]^+$ 270.1314, found 270.1310.

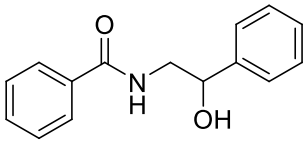
5. Late-Stage Functionalization of α-Sila Benzamides



***N*-formylbenzamide (4)**

Procedure modified from literature [9]:

In a dried Schlenk tube, *N*-[(triethylsilyl)methyl]benzamide (50 mg, 0.2 mmol), AgF (104 mg, 0.8 mmol), NBS (143 mg, 0.8 mmol) and THF (1 mL) was added under nitrogen atmosphere. After stirring at room temperature for 48 h, the reaction mixture was filtered through celite and removed the volatiles under vacuum. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound as a white solid (12 mg, 40% yield). Melting point: 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.68 (s, 1H), 9.39 (d, J = 9.7 Hz, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 164.0, 133.9, 131.1, 129.1, 127.9. IR (neat): 3393, 3190, 1644, 1577, 1405, 701 cm^{-1}. HRMS (APCI$^-$): calcd for $C_8H_6NO_2$ [M-H]$^-$ 148.0399, found 148.0392. Spectroscopic data are in accordance with those described in the literature.[8]

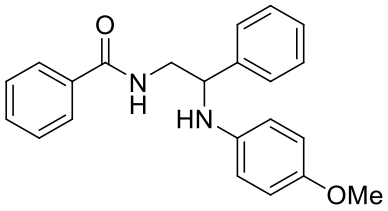


***N*-(2-hydroxy-2-phenylethyl)benzamide (5)**

Procedure modified from literature [11]:

In a dried Schlenk tube, *N*-[(triethylsilyl)methyl]benzamide (50 mg, 0.2 mmol), benzaldehyde (30 mg, 0.28 mmol), molecular sieves (4 Å, 100 mg) and THF (2.0 mL) were added under nitrogen atmosphere. Then, tetrabutylammonium fluoride (TBAF, 0.24 mL, 1 M solution in THF, 0.24 mmol) was added by syringe and the mixture was stirred at 60 °C for 20 h. After cooling to room temperature, 1 M HCl (3 mL) was

putted and the product was extracted with ethyl acetate. The organic layer was washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (19 mg, 38% yield). Melting point: 164–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.70 (m, 2H), 7.54–7.48 (m, 1H), 7.48–7.34 (m, 6H), 7.33–7.28 (m, 1H), 6.62 (brs, 1H), 5.01–4.93 (m, 1H), 3.96–3.90 (m, 1H), 3.56–3.49 (m, 1H), 3.36 (d, J = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 141.8, 134.1, 131.7, 128.61,128.60, 128.0, 127.0, 125.8, 73.8, 47.8. IR (neat): 3296, 1633, 1544, 1056, 913, 690 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1181, found 242.1179. Spectroscopic data are in accordance with those described in the literature.[10]

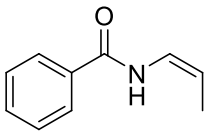


***N*-{2-[(4-methoxyphenyl)amino]-2-phenylethyl}benzamide (6)**

Procedure modified from literature [11]:

A solution of *N*-[(triethylsilyl)methyl]benzamide (50 mg, 0.2 mmol), (*E*)-*N*-benzylidene-4-methoxyaniline (55 mg, 0.26 mmol), and molecular sieves (4 Å, 100 mg) in THF (2 mL) was treated with TBAF (TBAF, 0.24 mL, 1 M solution in THF, 0.24 mmol) under nitrogen and the resulting solution was stirred at 60 °C for 24 h. The reaction was quenched with a saturated $NaHCO_3$ solution (4 mL) and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a white solid (30 mg, 43% yield). Melting point: 170–172 °C. ^{1}H NMR

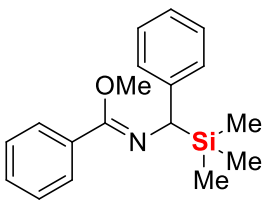
(400 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.42–7.33 (m, 6H), 7.30–7.25 (m, 1H), 6.67 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.8 Hz, 2H), 4.62 (s, 1H), 4.53 (dd, J = 7.6, 4.5 Hz, 1H), 3.87–3.72 (m, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 152.1, 141.4, 141.2, 134.2, 131.7, 128.9, 128.6, 127.6, 126.9, 126.6, 114.8, 114.7, 60.0, 55.7, 46.6. IR (neat): 3384, 1628, 1518, 1247, 1034, 813, 699 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{22}H_{23}N_2O_2$ $[M+H]^+$ 347.1760, found 347.1758.



(*Z*)-*N*-(prop-1-en-1-yl)benzamide (7)

Procedure modified from literature [7]:

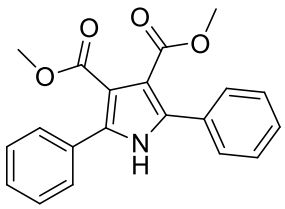
A solution of *N*-[1-(triethylsilyl)allyl]benzamide (56 mg, 0.2 mmol) in anhydrous Toluene (2 mL) was stirred at 110 ºC for 10 h. After cooling to room temperature, water (2 mL) was added and the product was extracted with ethyl acetate. The organic layer was washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel (EtOAc/PE =1/50) to afford the title compound as a pale yellow oil (26 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.5 Hz, 2H), 7.53 (s, 1H), 7.48 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 6.88 (t, J = 9.8 Hz, 1H), 4.93–4.82 (m, 1H), 1.64 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 134.0, 131.9, 128.8, 127.0, 122.3, 106.1, 11.0. IR (neat): 3389, 1646, 1577, 1403, 1143, 694 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{10}H_{12}NO$ $[M+H]^+$ 162.0919, found 162.0910. Spectroscopic data are in accordance with those described in the literature.[7]



Methyl *N*-[phenyl(trimethylsilyl)methyl]benzimidate (9)

Procedure modified from literature [12]:

To a solution of *N*-[α-(trimethylsilyl)benzyl]benzamide (283 mg, 1 mmol) in dichloromethane (10 mL), methyl trifluorometanesulfonate (329 mg, 2 mmol) was added and stirred at room temperature for 96 h. The reaction mixture was then washed with 1 M NaOH (10 mL) followed by dried over anhydrous Mg_2SO_4. After filtration, the volatiles were removed under vacuum to afford the title compound as a yellow oil (297 mg, quantitative yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.35 (m, 3H), 7.29–7.22 (m, 6H), 7.15–7.10 (m, 1H), 4.24 (s, 1H), 3.89 (s, 3H), –0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 143.7, 132.2, 129.2, 128.3, 128.0, 128.0, 125.9, 124.8, 57.9, 52.9, –3.7. IR (neat): 1659, 1492, 1246, 1117, 841, 700 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{18}H_{24}NOSi$ $[M+H]^+$ 298.1627, found 298.1623. Spectroscopic data are in accordance with those described in the literature.[12]



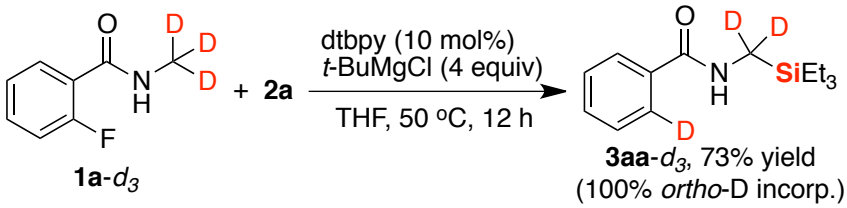
Dimethyl 2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate (8)

Procedure modified from literature [12]:

To a solution of Methyl *N*-[phenyl(trimethylsilyl)methyl]benzimidate (**9**) (60 mg, 0.2 mmoi) in dichloromethane (10 mL), dimethyl maleate (35 mg, 0.24 mmol) and trifluoro(phenyl)silane (39 mg, 0.24 mmol) were added at room temperature. After stirring for 48 h, the volatiles were removed unvacuum. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/50) to afford the title compound (65 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.06 (s, 1H), 7.52–7.50 (m, 4H), 7.38–7.32 (m, 6H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

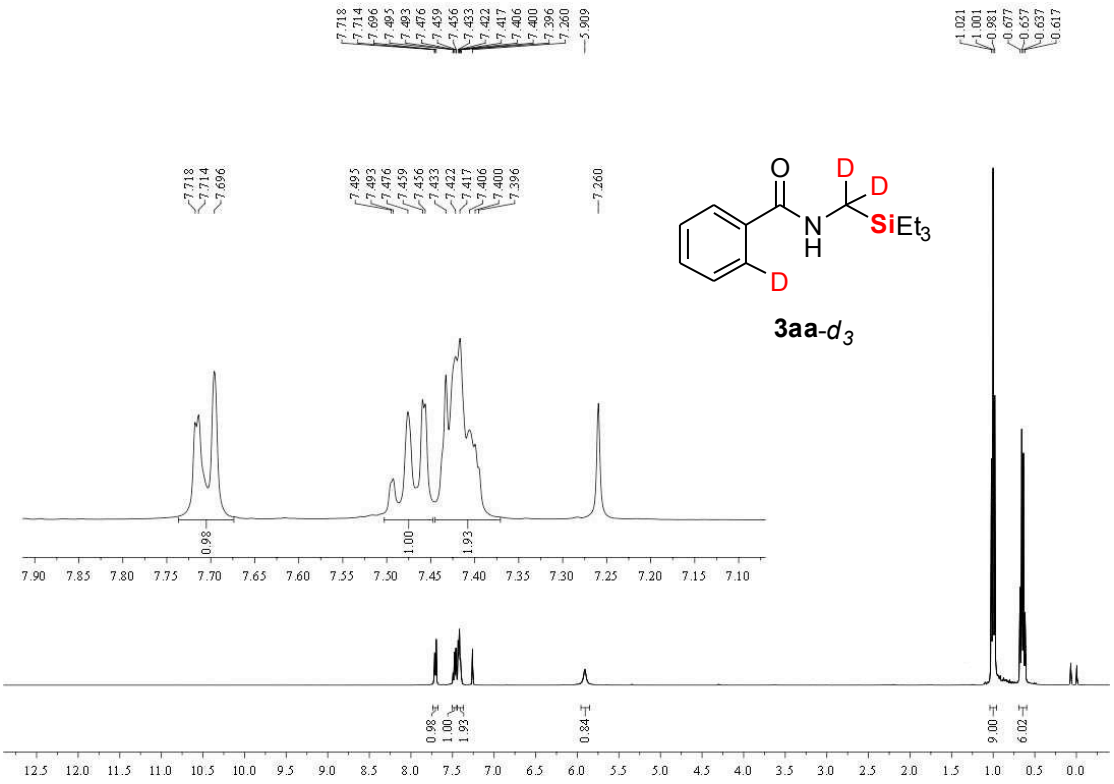
165.8, 134.6, 130.7, 128.4, 128.1, 113.9, 51.7. Spectroscopic data are in accordance with those described in the literature.[13]

6. The Measurement of [1,5]-D Transfer

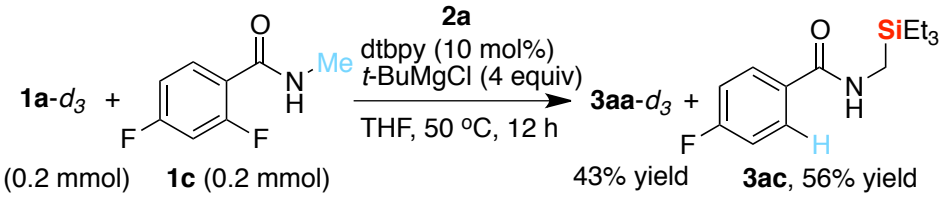


1a-d_3 **3aa-d_3**, 73% yield (100% *ortho*-D incorp.)

The general procedure was applied to **1a-d_3** (32 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound as a colorless oil (37 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.67 (m, 1H), 7.50–7.45 (m, 1H), 7.45–7.37 (m, 2H), 5.91 (brs, 1H), 1.00 (t, J = 7.9 Hz, 9H), 0.65 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 135.1, 131.1, 128.6, 128.5, 126.6, 7.3, 2.6. IR (neat): 3299, 1627, 1532, 1315, 1017, 739 cm^{-1}. HRMS (APCI$^+$): calcd for $C_{14}H_{21}D_3NOSi$ $[M+H]^+$ 253.1816, found 253.1812.

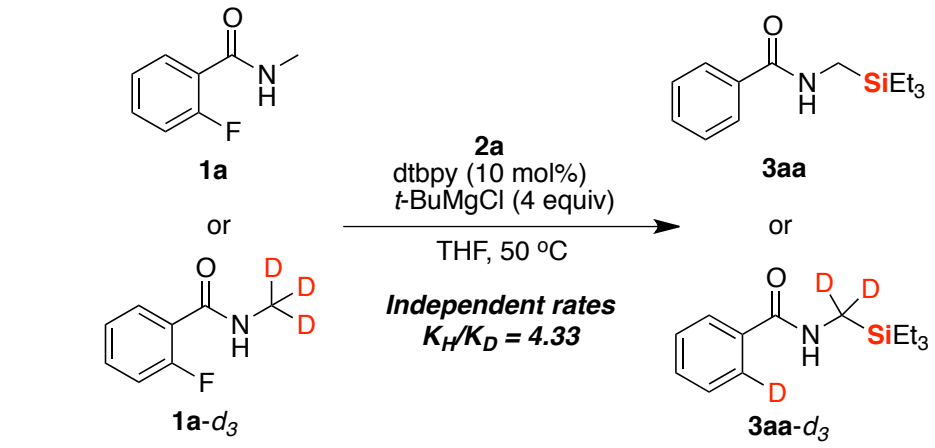


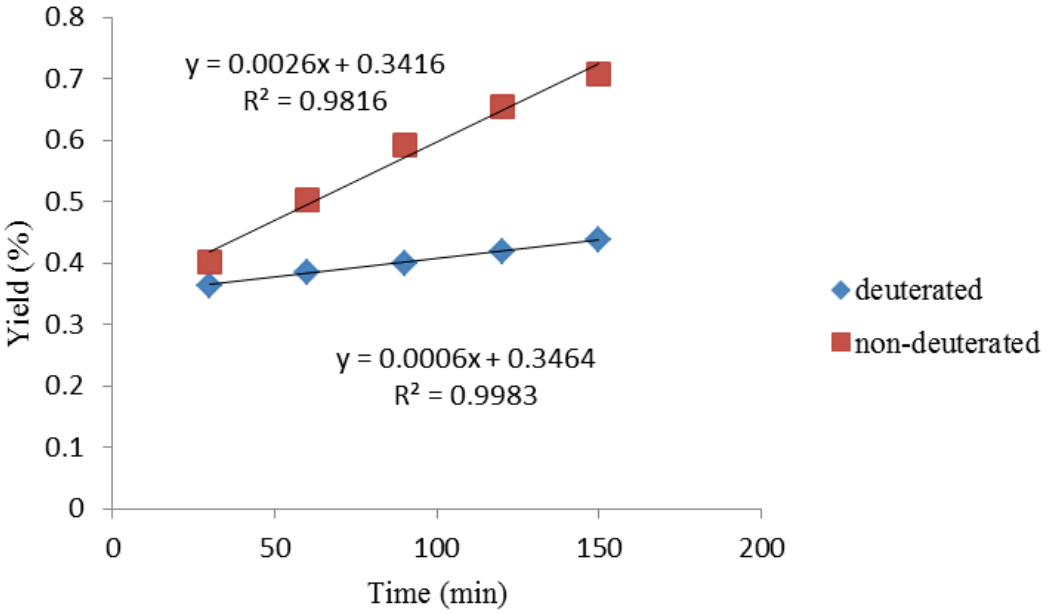
7. H/D crossover experiment



The general procedure was applied to **1a-*d*$_3$** (32 mg, 0.2 mmol), **1c** (35 mg, 0.2 mmol) triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/100) to afford the **3aa**-d_3 (43% yield) and **3ac** (56% yield).

8. Kinetic Isotope Effect on the Silylation of C(sp^3)–H Bond





The general procedure was applied to **1a** (31 mg, 0.2 mmol) or **1a-*d*$_3$** (32 mg, 0.2 mmol), triethylchlorosilane (121 mg, 0.8 mmol), *tert*-butylmagnesium chloride (0.8 mL, 1.0 M in THF, 0.8 mmol) and dtbpy (6 mg, 0.02 mmol) at 50 °C for designated time (30 min, 60 min, 90 min, 120 min, 150 min). Then the reaction mixture was cooled to room temperature and quenched with a solution of NH_4Cl. The yield was determined by GC analysis. A value of K_H/K_D=4.33 was obtained.

9. X-Ray Crystal Structure of 3ba

Product 3ba:

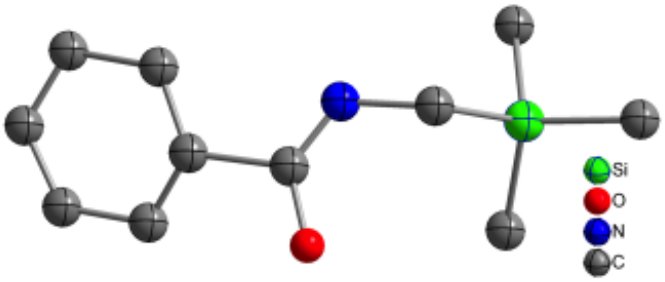


Table S6. Crystal data and structure refinement for 3ba.

Identification code	1
Empirical formula	$C_{11}H_{17}NOSi$
Formula weight	207.35
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, Pc
Unit cell dimensions	a = 10.178(4) A alpha = 90 deg.
	b = 10.104(4) A beta = 108.216(6) deg.
	c = 12.720(5) A gamma = 90 deg.
Volume	1242.5(8) A^3
Z, Calculated density	4, 1.108 Mg/m^3
Absorption coefficient	0.161 mm^-1
F(000)	448
Crystal size	? x ? x ? mm
Theta range for data collection	2.02 to 24.64 deg.
Limiting indices	-11<=h<=11, -11<=k<=11, -13<=l<=14
Reflections collected / unique	9597 / 3768 [R(int) = 0.0254]

Completeness to theta = 24.64	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3768 / 26 / 260
Goodness-of-fit on F^2	1.261
Final R indices [I>2sigma(I)]	R1 = 0.1330, wR2 = 0.3229
R indices (all data)	R1 = 0.1578, wR2 = 0.3530
Absolute structure parameter	0.4(5)
Largest diff. peak and hole	1.792 and -0.518 e.A^-3

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3ba.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Si(1)	12145(2)	9948(2)	7387(2)	41(1)
O(1)	8943(12)	11938(7)	7311(10)	98(3)
N(1)	9338(8)	9834(8)	7243(7)	50(2)
C(2)	13194(15)	9992(9)	6414(12)	71(3)
C(1)	12541(12)	11393(12)	8328(10)	74(3)
C(3)	12530(12)	8431(11)	8222(11)	77(4)
C(4)	10254(10)	9940(7)	6545(8)	42(2)
C(5)	8804(13)	10766(9)	7536(11)	74(4)
C(6)	7828(13)	10528(10)	8299(9)	62(3)
C(11)	7700(17)	11462(12)	8948(16)	102(5)
C(10)	6875(16)	11195(15)	9617(14)	97(4)
C(9)	6382(11)	10020(9)	9750(11)	59(3)

C(8)	6659(16)	8985(15)	9231(15)	99(4)
C(7)	7399(14)	9295(12)	8353(10)	77(4)
Si(2)	5630(3)	4969(2)	5759(2)	42(1)
O(2)	8824(12)	6923(6)	7276(10)	98(3)
N(2)	8428(8)	4822(8)	7012(7)	50(2)
C(12)	5267(11)	6406(12)	6517(11)	70(3)
C(14)	5207(12)	3430(12)	6381(12)	80(4)
C(13)	4573(14)	5054(9)	4251(10)	66(3)
C(15)	7529(10)	4954(7)	5865(9)	44(2)
C(16)	8959(13)	5766(9)	7569(13)	77(4)
C(17)	9950(12)	5534(10)	8833(10)	62(3)
C(18)	10090(17)	6446(12)	9567(16)	104(5)
C(19)	10855(14)	6202(13)	10631(13)	89(4)
C(20)	11404(11)	5013(9)	11014(10)	58(3)
C(21)	11078(18)	3965(15)	10331(14)	111(5)
C(22)	10377(14)	4290(12)	9102(11)	77(3)

Table S8. Bond lengths [A] and angles [deg] for 3ba.

Si(1)-C(3)	1.836(10)
Si(1)-C(1)	1.850(10)
Si(1)-C(2)	1.872(11)
Si(1)-C(4)	1.887(10)
O(1)-C(5)	1.236(11)
N(1)-C(5)	1.203(14)
N(1)-C(4)	1.480(14)
N(1)-H(1)	0.8600

C(2)-H(2A)	0.9600
C(2)-H(2B)	0.9600
C(2)-H(2C)	0.9600
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(3)-H(3A)	0.9600
C(3)-H(3B)	0.9600
C(3)-H(3C)	0.9600
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.610(18)
C(6)-C(11)	1.287(18)
C(6)-C(7)	1.329(18)
C(11)-C(10)	1.40(2)
C(11)-H(11)	0.9300
C(10)-C(9)	1.321(17)
C(10)-H(10)	0.9300
C(9)-C(8)	1.313(18)
C(9)-H(9)	0.9300
C(8)-C(7)	1.56(2)
C(8)-H(8)	0.9300
C(7)-H(7)	0.9300
Si(2)-C(12)	1.844(10)
Si(2)-C(14)	1.855(10)
Si(2)-C(13)	1.885(12)
Si(2)-C(15)	1.894(10)

O(2)-C(16)	1.222(11)
N(2)-C(16)	1.210(15)
N(2)-C(15)	1.466(14)
N(2)-H(2)	0.8600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.626(18)
C(17)-C(18)	1.287(19)
C(17)-C(22)	1.339(17)
C(18)-C(19)	1.36(2)
C(18)-H(18)	0.9300
C(19)-C(20)	1.350(16)
C(19)-H(19)	0.9300
C(20)-C(21)	1.344(18)
C(20)-H(20)	0.9300
C(21)-C(22)	1.54(2)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300

C(3)-Si(1)-C(1)	108.7(7)
C(3)-Si(1)-C(2)	109.9(5)
C(1)-Si(1)-C(2)	110.8(6)
C(3)-Si(1)-C(4)	108.7(5)
C(1)-Si(1)-C(4)	110.4(4)
C(2)-Si(1)-C(4)	108.4(6)
C(5)-N(1)-C(4)	124.0(10)
C(5)-N(1)-H(1)	118.0
C(4)-N(1)-H(1)	118.0
Si(1)-C(2)-H(2A)	109.5
Si(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
Si(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
Si(1)-C(1)-H(1A)	109.5
Si(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
Si(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
Si(1)-C(3)-H(3A)	109.5
Si(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
Si(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5

N(1)-C(4)-Si(1)	112.4(7)
N(1)-C(4)-H(4A)	109.1
Si(1)-C(4)-H(4A)	109.1
N(1)-C(4)-H(4B)	109.1
Si(1)-C(4)-H(4B)	109.1
H(4A)-C(4)-H(4B)	107.9
N(1)-C(5)-O(1)	125.7(14)
N(1)-C(5)-C(6)	119.6(9)
O(1)-C(5)-C(6)	114.8(11)
C(11)-C(6)-C(7)	123.6(12)
C(11)-C(6)-C(5)	118.8(10)
C(7)-C(6)-C(5)	116.5(10)
C(6)-C(11)-C(10)	116.8(13)
C(6)-C(11)-H(11)	121.6
C(10)-C(11)-H(11)	121.6
C(9)-C(10)-C(11)	125.2(14)
C(9)-C(10)-H(10)	117.4
C(11)-C(10)-H(10)	117.4
C(8)-C(9)-C(10)	120.1(13)
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-H(9)	119.9
C(9)-C(8)-C(7)	115.3(12)
C(9)-C(8)-H(8)	122.3
C(7)-C(8)-H(8)	122.3
C(6)-C(7)-C(8)	117.7(10)
C(6)-C(7)-H(7)	121.2
C(8)-C(7)-H(7)	121.2

C(12)-Si(2)-C(14)	109.0(7)
C(12)-Si(2)-C(13)	110.6(5)
C(14)-Si(2)-C(13)	109.7(6)
C(12)-Si(2)-C(15)	109.6(4)
C(14)-Si(2)-C(15)	109.3(4)
C(13)-Si(2)-C(15)	108.6(6)
C(16)-N(2)-C(15)	122.5(10)
C(16)-N(2)-H(2)	118.8
C(15)-N(2)-H(2)	118.8
Si(2)-C(12)-H(12A)	109.5
Si(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
Si(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
Si(2)-C(14)-H(14A)	109.5
Si(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(2)-C(13)-H(13A)	109.5
Si(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
Si(2)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

N(2)-C(15)-Si(2)	112.1(7)
N(2)-C(15)-H(15A)	109.2
Si(2)-C(15)-H(15A)	109.2
N(2)-C(15)-H(15B)	109.2
Si(2)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
N(2)-C(16)-O(2)	126.1(15)
N(2)-C(16)-C(17)	119.4(9)
O(2)-C(16)-C(17)	114.5(12)
C(18)-C(17)-C(22)	122.2(12)
C(18)-C(17)-C(16)	120.5(11)
C(22)-C(17)-C(16)	116.1(9)
C(17)-C(18)-C(19)	119.5(14)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(20)-C(19)-C(18)	124.4(13)
C(20)-C(19)-H(19)	117.8
C(18)-C(19)-H(19)	117.8
C(21)-C(20)-C(19)	118.5(13)
C(21)-C(20)-H(20)	120.7
C(19)-C(20)-H(20)	120.7
C(20)-C(21)-C(22)	115.5(12)
C(20)-C(21)-H(21)	122.2
C(22)-C(21)-H(21)	122.2
C(17)-C(22)-C(21)	118.1(10)
C(17)-C(22)-H(22)	121.0

C(21)-C(22)-H(22)	121.0

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters (A^2 x 10^3) for 3ba.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	44(1)	38(1)	40(2)	-1(1)	13(1)	0(1)
O(1)	102(6)	51(4)	142(8)	9(5)	42(6)	-3(4)
N(1)	47(5)	60(5)	38(5)	-9(3)	6(4)	15(4)
C(2)	87(9)	76(8)	67(9)	1(5)	48(7)	1(5)
C(1)	70(7)	72(7)	64(8)	-26(6)	1(6)	12(5)
C(3)	67(7)	66(7)	95(10)	36(6)	21(7)	1(5)
C(4)	43(5)	47(5)	32(5)	1(3)	4(4)	0(3)
C(5)	70(7)	38(5)	88(9)	23(6)	-13(6)	-8(5)
C(6)	86(8)	44(5)	46(6)	-11(4)	5(5)	-17(5)
C(11)	105(10)	53(7)	155(14)	16(8)	52(10)	18(6)
C(10)	94(7)	94(7)	117(9)	10(6)	53(7)	18(6)
C(9)	44(5)	70(7)	69(8)	0(5)	25(5)	2(4)
C(8)	94(7)	83(7)	133(9)	-23(6)	54(7)	-24(6)
C(7)	110(9)	55(7)	61(7)	-19(5)	21(7)	18(6)
Si(2)	45(1)	38(1)	42(2)	-1(1)	14(1)	1(1)
O(2)	106(6)	46(4)	137(8)	15(5)	32(6)	3(4)
N(2)	47(5)	58(5)	48(5)	-19(4)	21(4)	-17(4)
C(12)	56(6)	84(8)	80(8)	-32(6)	34(6)	0(5)

C(14)	70(7)	78(8)	95(10)	39(7)	30(7)	-3(6)
C(13)	79(8)	71(7)	39(7)	-3(4)	5(6)	0(5)
C(15)	47(5)	44(5)	45(6)	-6(4)	19(4)	3(3)
C(16)	73(7)	48(6)	132(12)	42(7)	65(8)	14(5)
C(17)	92(8)	38(5)	73(8)	1(5)	49(7)	18(5)
C(18)	107(10)	56(7)	143(15)	2(8)	31(10)	-28(7)
C(19)	90(7)	73(6)	85(8)	-2(6)	-1(6)	-15(6)
C(20)	44(5)	65(7)	51(7)	-1(4)	-3(5)	1(4)
C(21)	121(9)	76(7)	115(9)	-9(6)	7(7)	48(6)
C(22)	99(9)	66(7)	72(9)	-29(6)	34(7)	-16(6)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3ba.

	x	y	z	U(eq)
H(1)	9177	9058	7453	60
H(2A)	14160	10022	6830	107
H(2B)	12953	10764	5953	107
H(2C)	13008	9213	5959	107
H(1A)	12013	11338	8834	110
H(1B)	12305	12192	7902	110
H(1C)	13509	11398	8736	110
H(3A)	12080	8466	8782	115
H(3B)	13511	8356	8567	115
H(3C)	12200	7678	7754	115
H(4A)	10039	10748	6113	51

H(4B)	10077	9201	6033	51
H(11)	8136	12275	8971	122
H(10)	6654	11902	10000	116
H(9)	5838	9924	10212	71
H(8)	6431	8128	9377	119
H(7)	7535	8639	7885	92
H(2)	8583	4045	7300	60
H(12A)	5938	6444	7240	106
H(12B)	4358	6321	6586	106
H(12C)	5315	7203	6119	106
H(14A)	5833	3330	7118	120
H(14B)	5293	2684	5940	120
H(14C)	4276	3481	6407	120
H(13A)	3608	4993	4182	99
H(13B)	4824	4334	3860	99
H(13C)	4748	5878	3945	99
H(15A)	7702	4223	5432	53
H(15B)	7753	5768	5555	53
H(18)	9670	7265	9369	124
H(19)	11011	6901	11130	107
H(20)	11995	4921	11734	69
H(21)	11263	3100	10585	133
H(22)	10253	3642	8560	93

Table S11. Torsion angles [deg] for 3ba.

C(5)-N(1)-C(4)-Si(1)	96.4(10)

C(3)-Si(1)-C(4)-N(1)	57.6(7)
C(1)-Si(1)-C(4)-N(1)	-61.5(7)
C(2)-Si(1)-C(4)-N(1)	177.0(5)
C(4)-N(1)-C(5)-O(1)	-0.6(17)
C(4)-N(1)-C(5)-C(6)	-179.9(8)
N(1)-C(5)-C(6)-C(11)	153.3(12)
O(1)-C(5)-C(6)-C(11)	-26.1(17)
N(1)-C(5)-C(6)-C(7)	-15.4(15)
O(1)-C(5)-C(6)-C(7)	165.3(10)
C(7)-C(6)-C(11)-C(10)	-10(2)
C(5)-C(6)-C(11)-C(10)	-178.2(11)
C(6)-C(11)-C(10)-C(9)	10(2)
C(11)-C(10)-C(9)-C(8)	0(3)
C(10)-C(9)-C(8)-C(7)	-8(2)
C(11)-C(6)-C(7)-C(8)	2.0(19)
C(5)-C(6)-C(7)-C(8)	170.1(11)
C(9)-C(8)-C(7)-C(6)	8(2)
C(16)-N(2)-C(15)-Si(2)	-96.8(9)
C(12)-Si(2)-C(15)-N(2)	61.9(7)
C(14)-Si(2)-C(15)-N(2)	-57.5(8)
C(13)-Si(2)-C(15)-N(2)	-177.2(6)
C(15)-N(2)-C(16)-O(2)	0.7(17)
C(15)-N(2)-C(16)-C(17)	-179.7(8)
N(2)-C(16)-C(17)-C(18)	-152.7(12)
O(2)-C(16)-C(17)-C(18)	27.0(16)
N(2)-C(16)-C(17)-C(22)	15.0(14)
O(2)-C(16)-C(17)-C(22)	-165.3(10)

C(22)-C(17)-C(18)-C(19)	9(2)
C(16)-C(17)-C(18)-C(19)	176.0(11)
C(17)-C(18)-C(19)-C(20)	-6(2)
C(18)-C(19)-C(20)-C(21)	-6(2)
C(19)-C(20)-C(21)-C(22)	13(2)
C(18)-C(17)-C(22)-C(21)	-1(2)
C(16)-C(17)-C(22)-C(21)	-168.6(12)
C(20)-C(21)-C(22)-C(17)	-10(2)

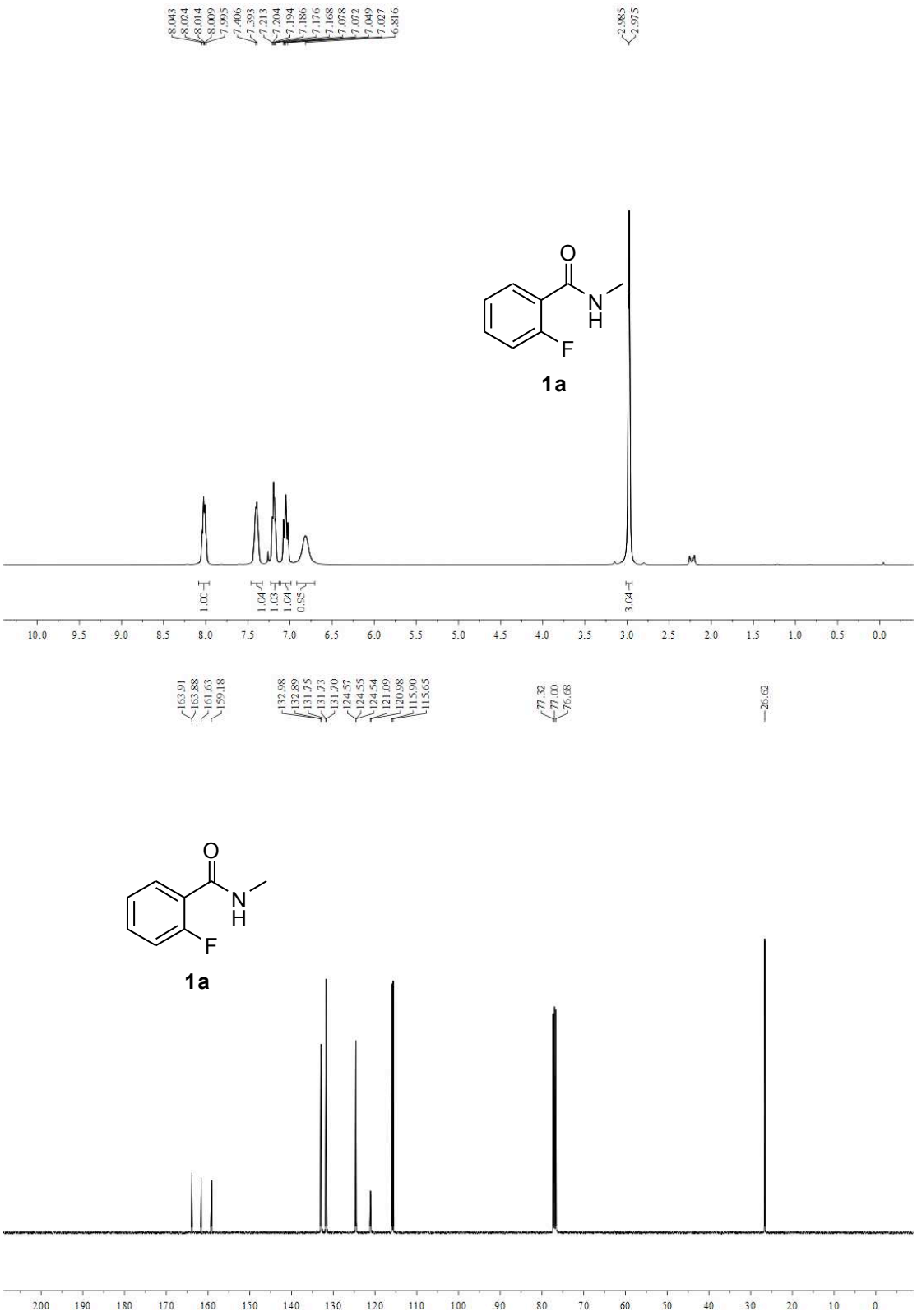
Symmetry transformations used to generate equivalent atoms:

Supplementary References

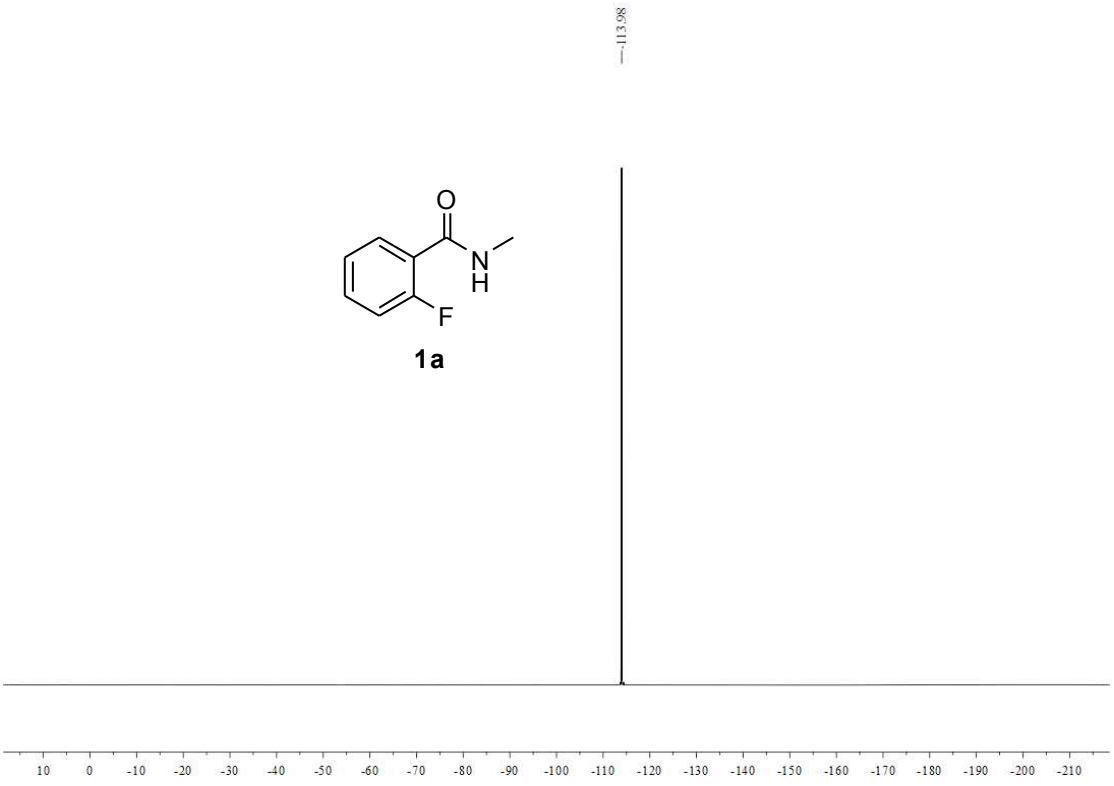
1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, 2923–2925.
2. Galan, J. F.; Brown, J.; Wildin, J. L.; Liu, Z.; Liu, D.; Moyna, G.; Pophristic, V. *J. Phys. Chem. B.* **2009**, 113, 12809–12815.
3. Du, Y.; Hyster, T. K.; Rovis, T. *Chem. Commun.* **2011**, 47, 12074–12076.
4. Yu, D.-G.; Gensch. T.; Azambuja, F. D.; Vásquez-Céspedes, S.; Glorius, F. *J. Am. Chem. Soc.* **2014**, 136, 17722−17725.
5. Reddy, K. R.; Maheswari, C. U.; Venkateshwar, M.; Kantam, M. L. *Eur. J. Org. Chem.* **2008**, 3619–3622.
6. Yedage, S. L.; D'silva, D. S.; Bhanage, B. M. *RSC Adv*, **2015**, 5, 80441–80449.
7. Lin, S.; Yang, Z.-Q.; Kwok, B. H. B.; Koldobskiy, M.; Crews, C. M.; Danishefsky, S. *J. Am. Chem. Soc.* **2004**, 126, 6347–6355.
8. Niu, Z.; Lin, S.; Dong, Z.; Sun, H.; Liang, F.; Zhang, J. *Org. Biomol. Chem.* **2013**, 11, 2460–2465.

9. Chernyak, N.; Dudnik, A. S.; Huang, C.; Gevorgyan, V. *J. Am. Chem. Soc.* **2010**, 132, 8270–8272.
10. Cardus, G. J.; Carnell, A. J.; Trauthwein, H.; Riermeir, T.; *Tetrahedron: Asymmetry* **2004**, 15, 239–243.
11. Leiendecker, M.; Hsiao, C.-C.; Guo, L.; Alandini, N.; Rueping, M. *Angew. Chem., Int. Ed.* **2014**, 53, 12912–12915.
12. Washizuka, K. I.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron*. **1999**, 55, 12969–12976.
13. Xuan, J.; Xia, X.-D.; Zeng, T.-T.; Feng, Z.-J.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2014**, 53, 5653–5656.

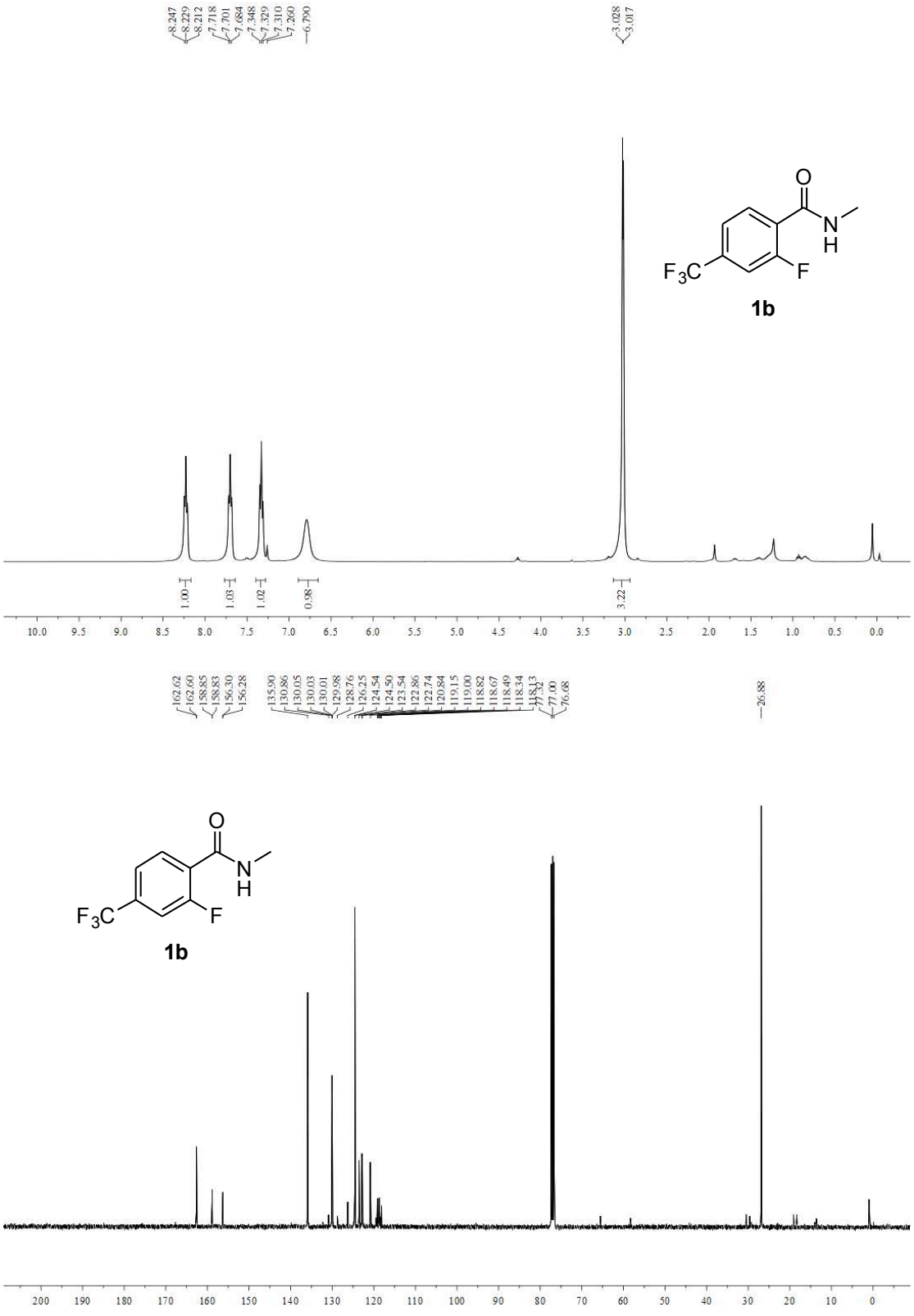
10. ^{1}H, ^{13}C and ^{19}F NMR Spectra



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1a

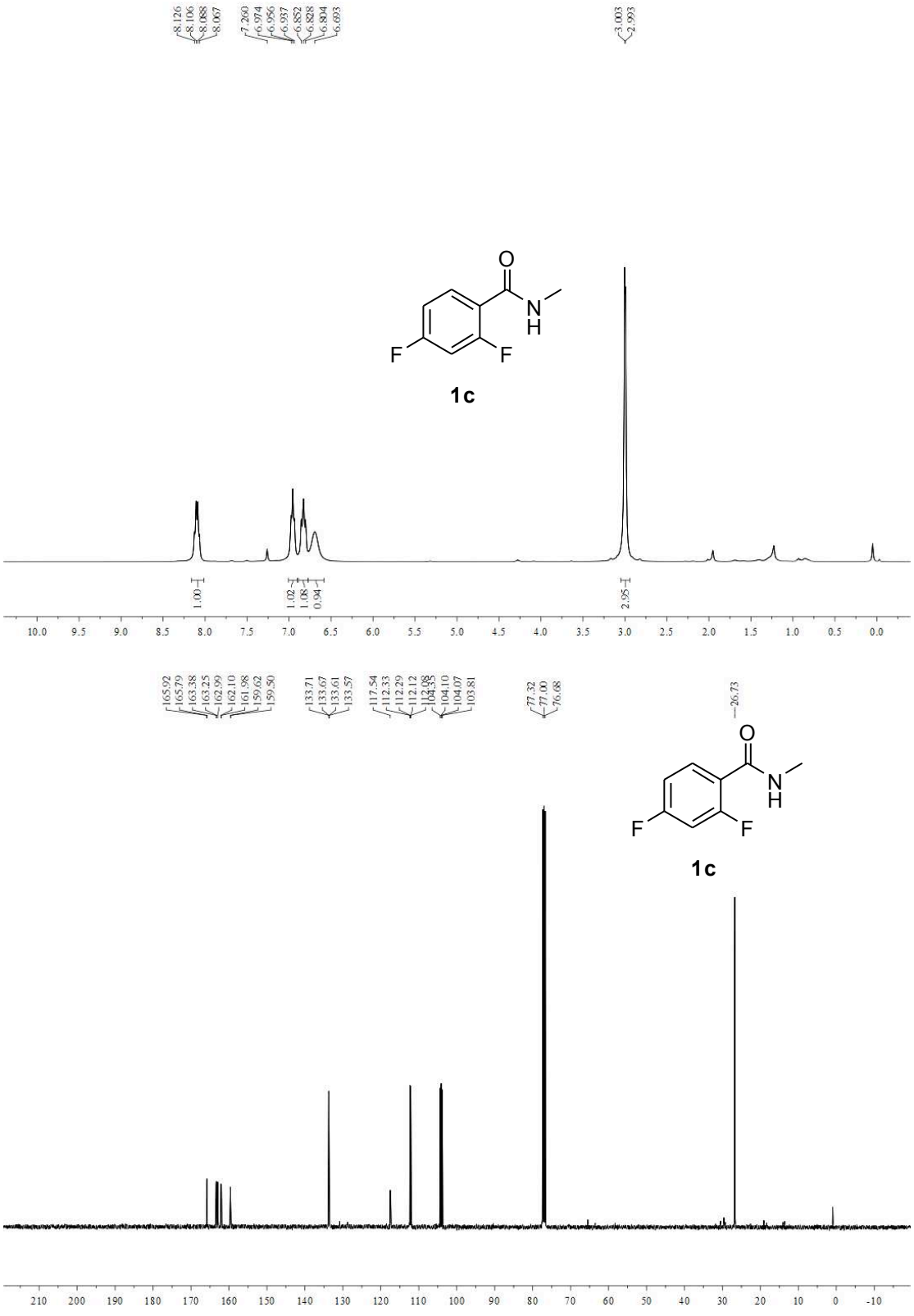


^{19}F NMR spectrum in $CDCl_3$ for compound 1a



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1b

^{19}F NMR spectrum in $CDCl_3$ for compound 1b



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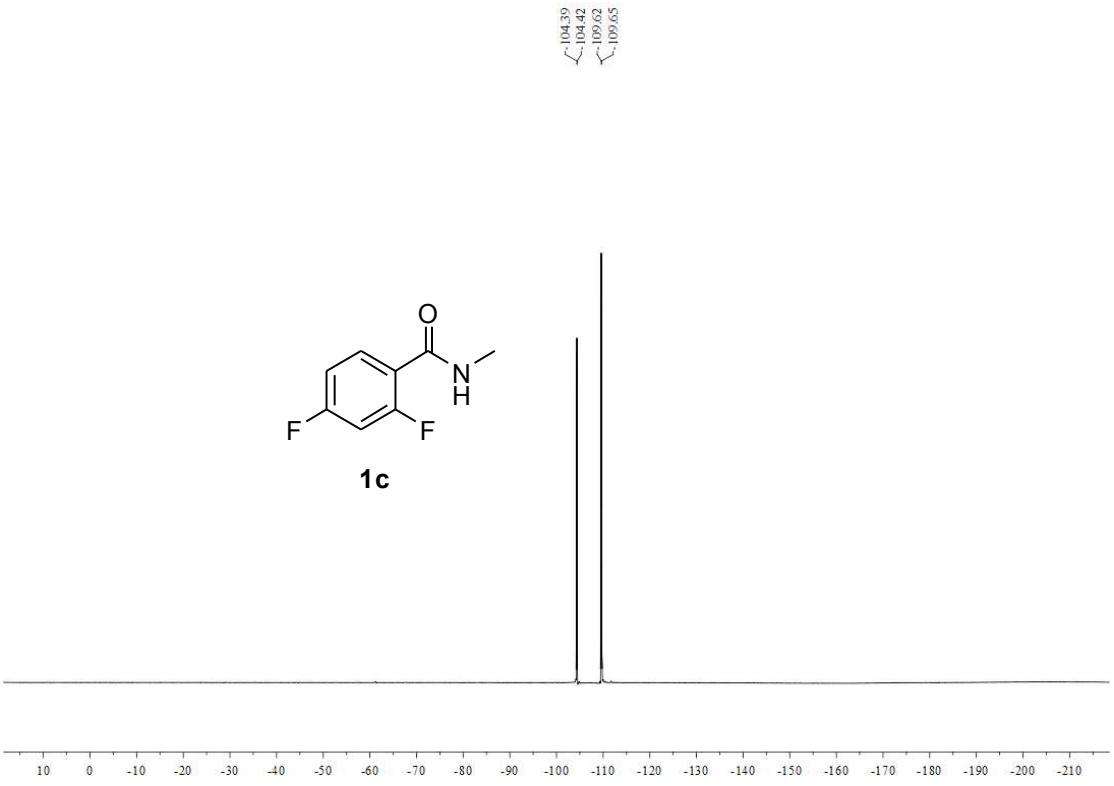
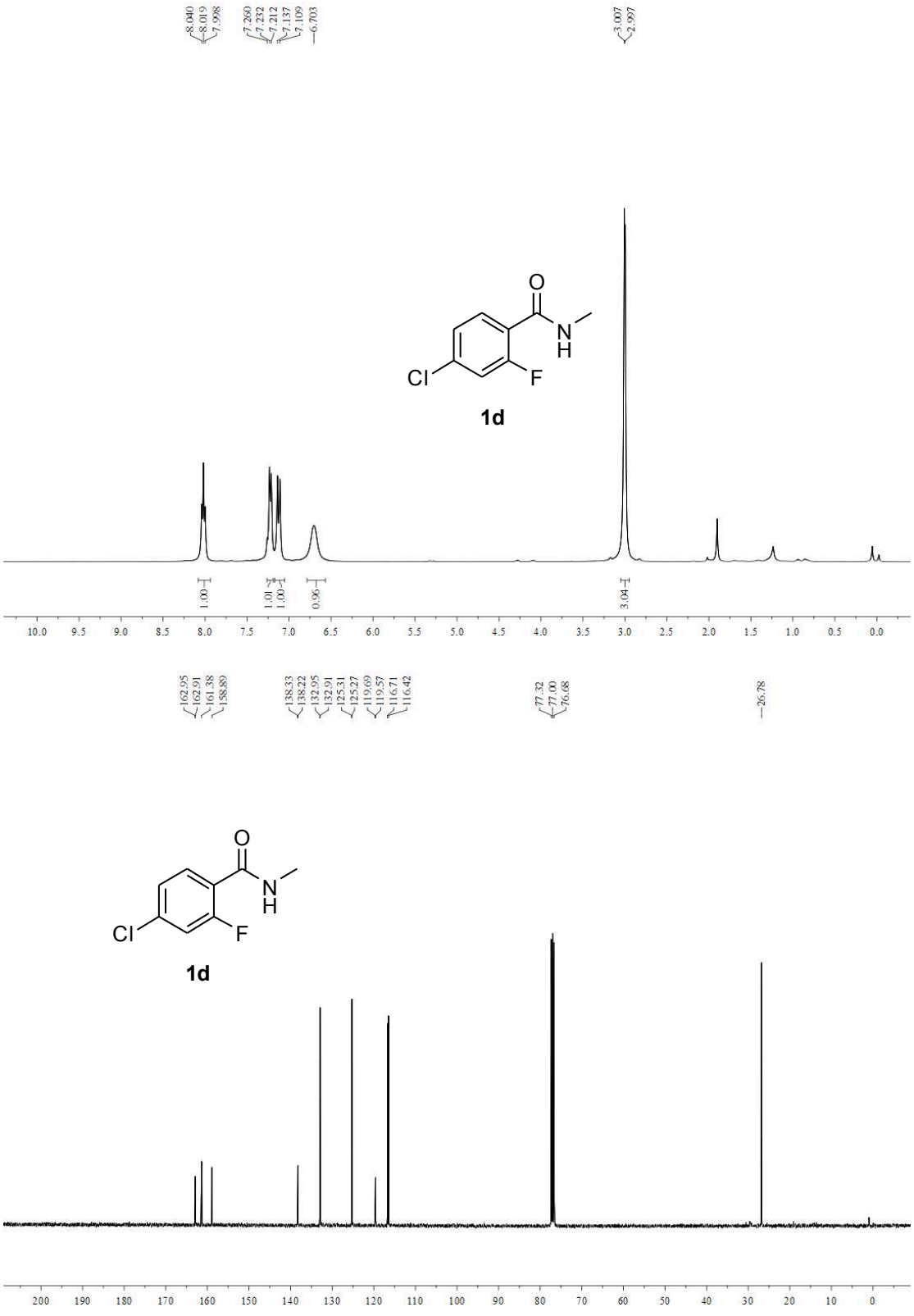
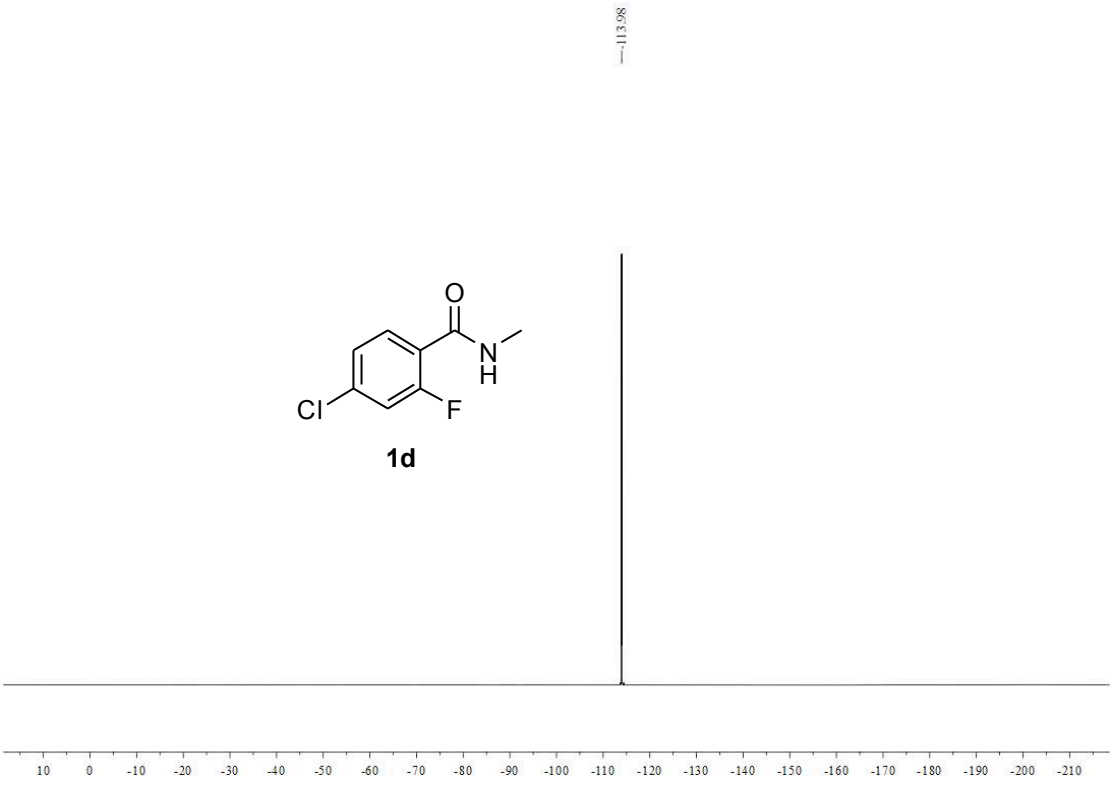


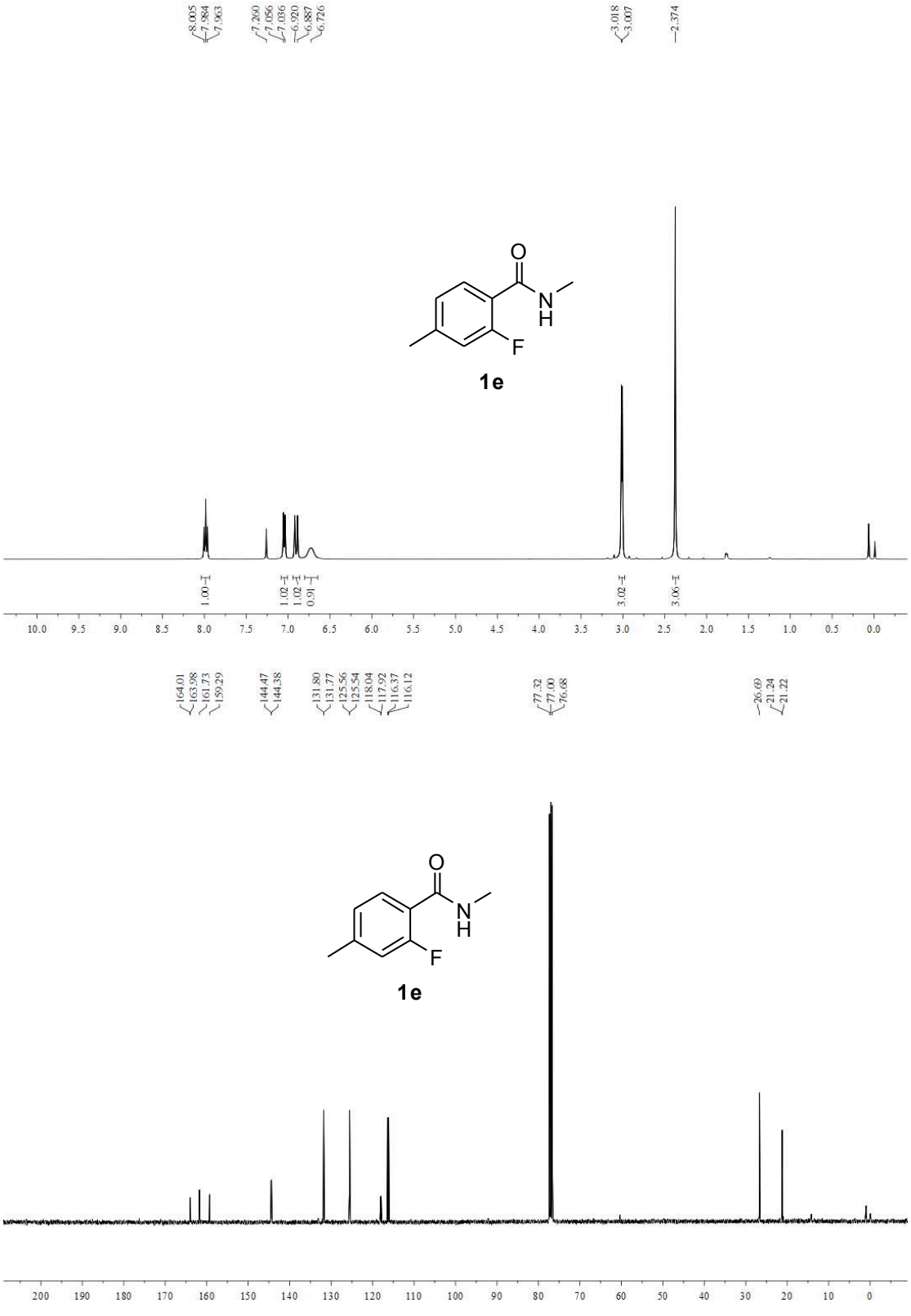
^{19}F NMR spectrum in $CDCl_3$ for compound 1c



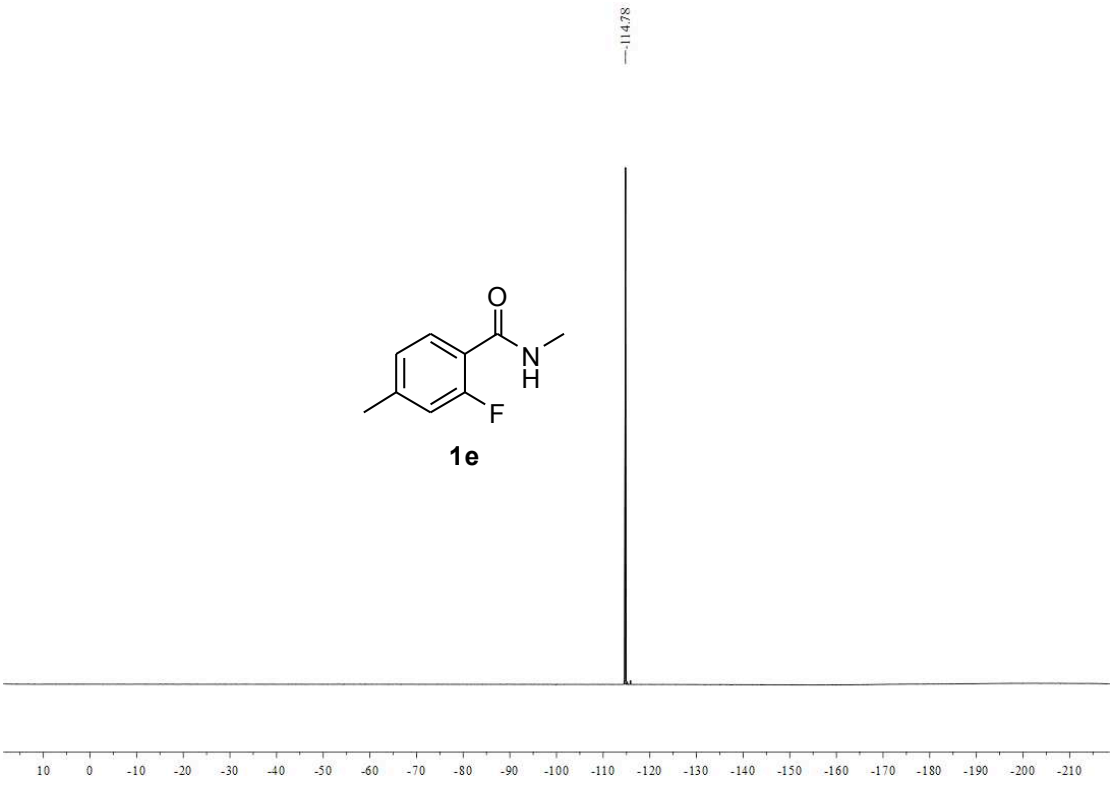
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1d



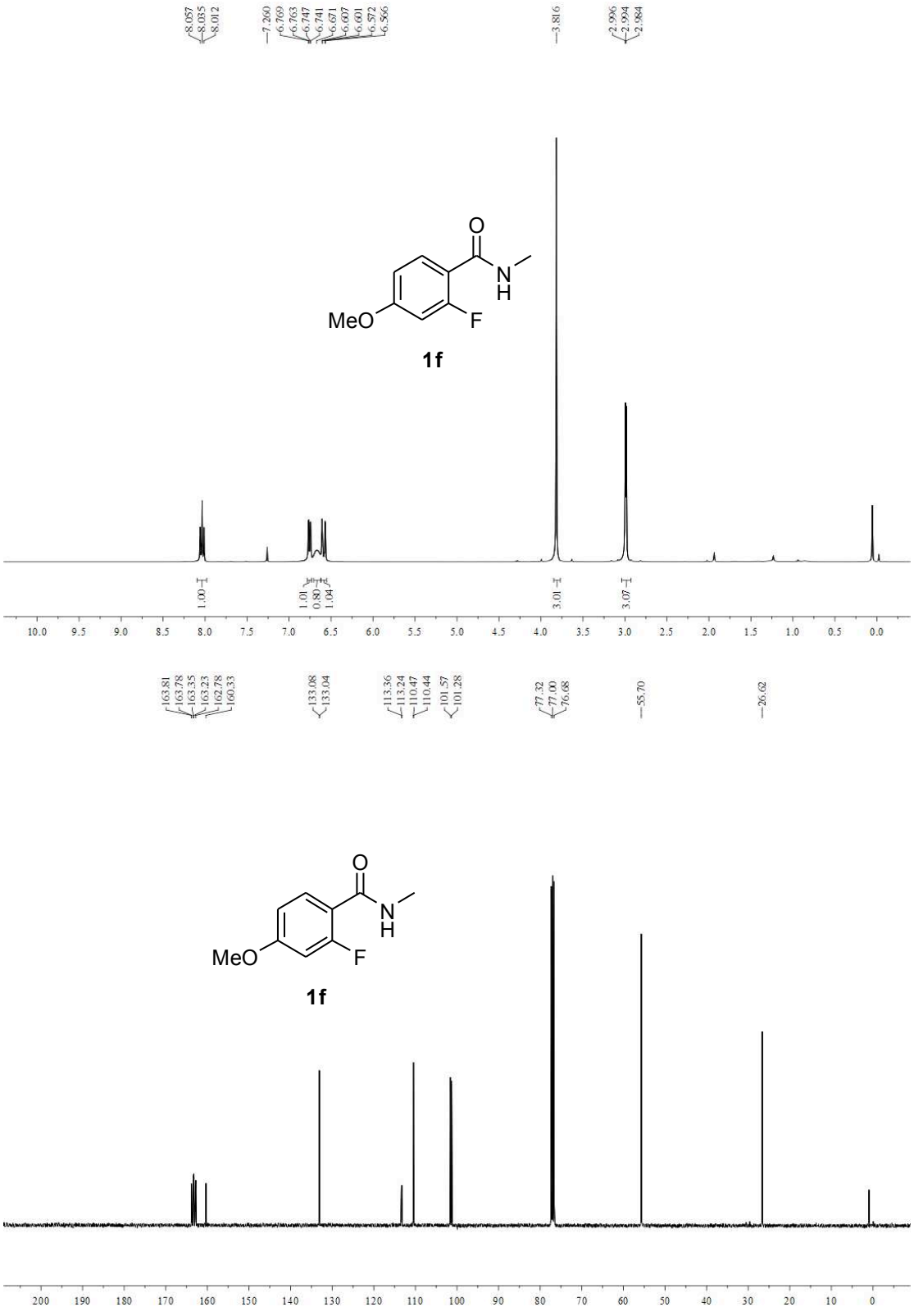
^{19}F NMR spectrum in $CDCl_3$ for compound 1d



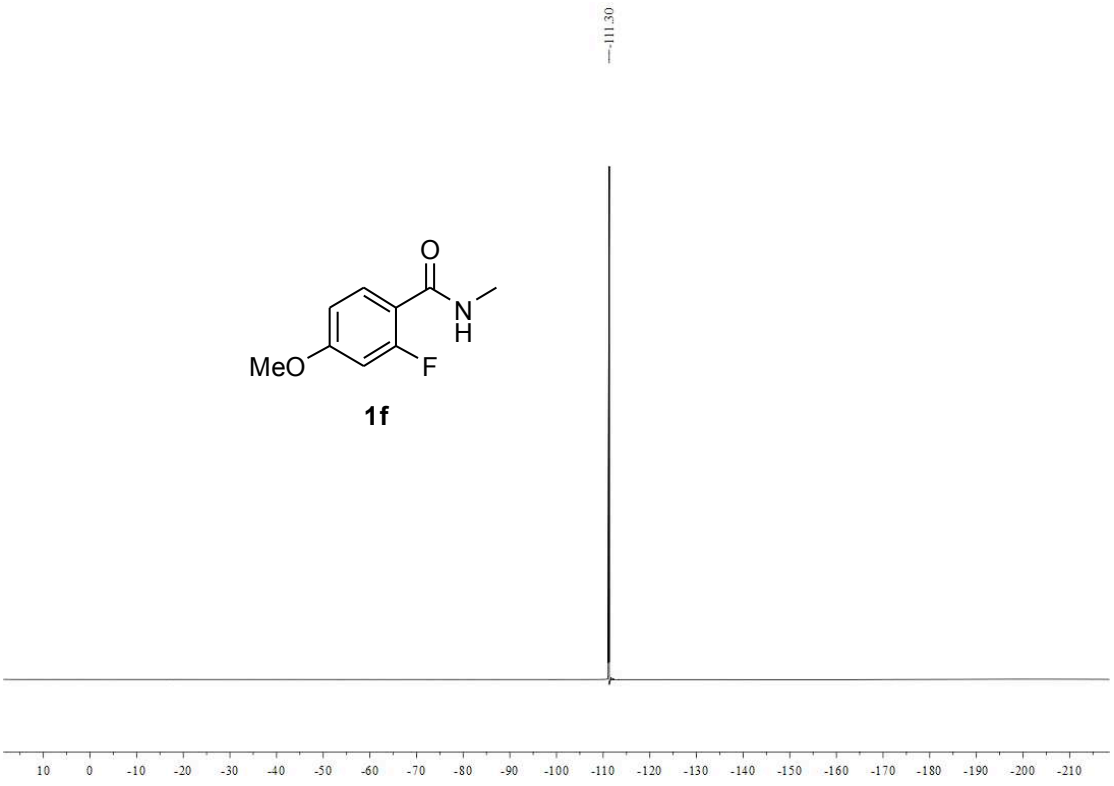
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1e



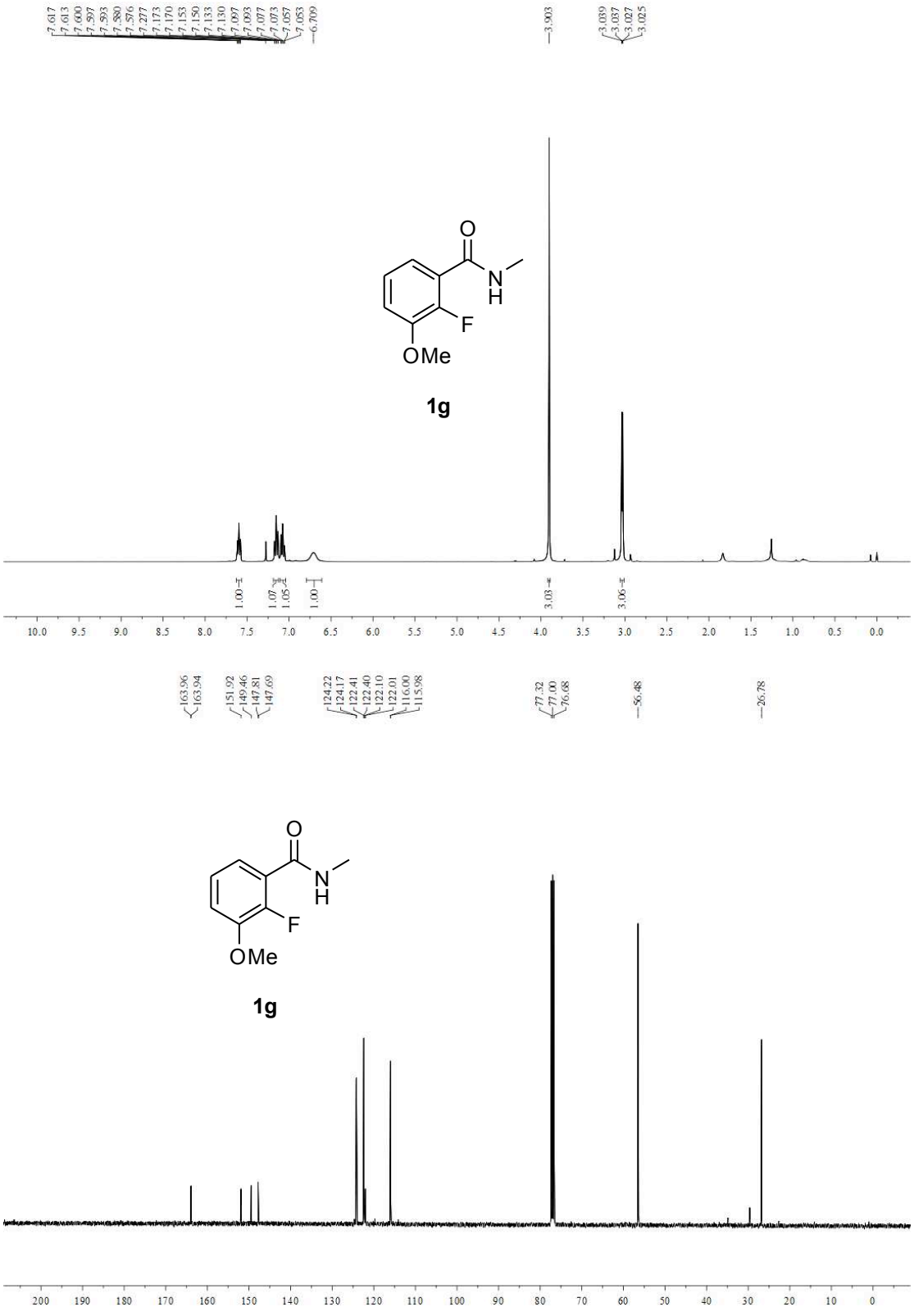
^{19}F NMR spectrum in $CDCl_3$ for compound 1e



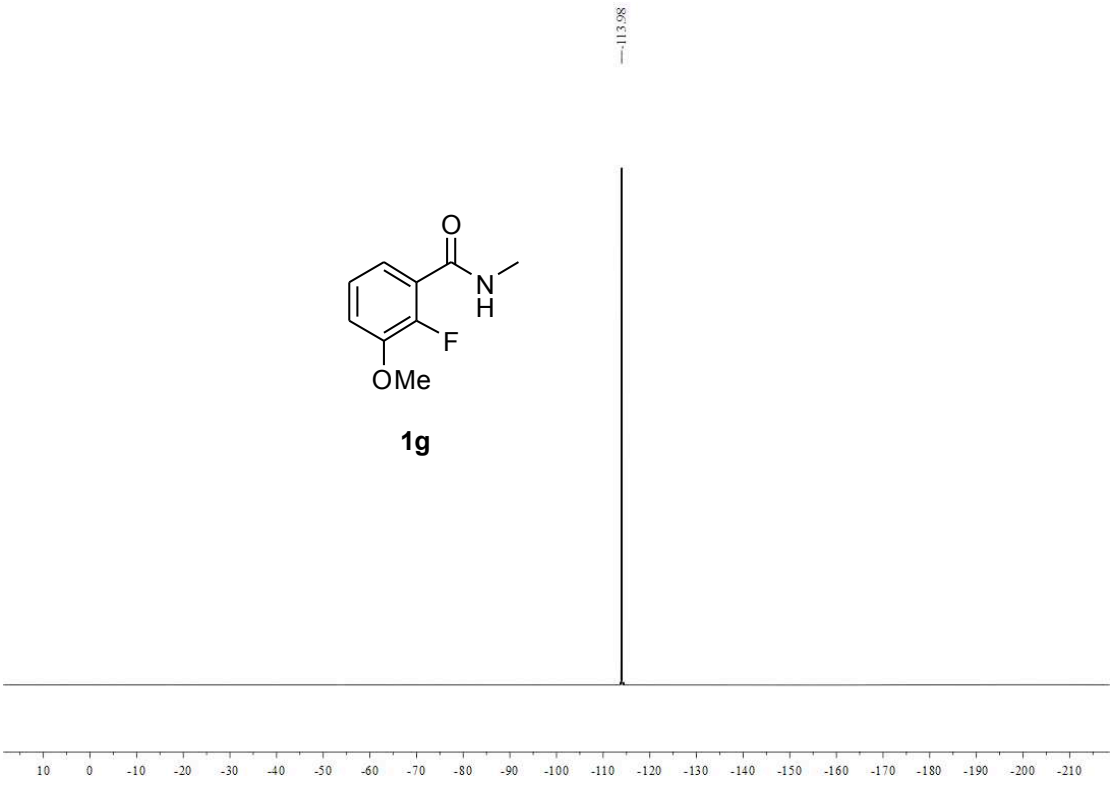
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1f



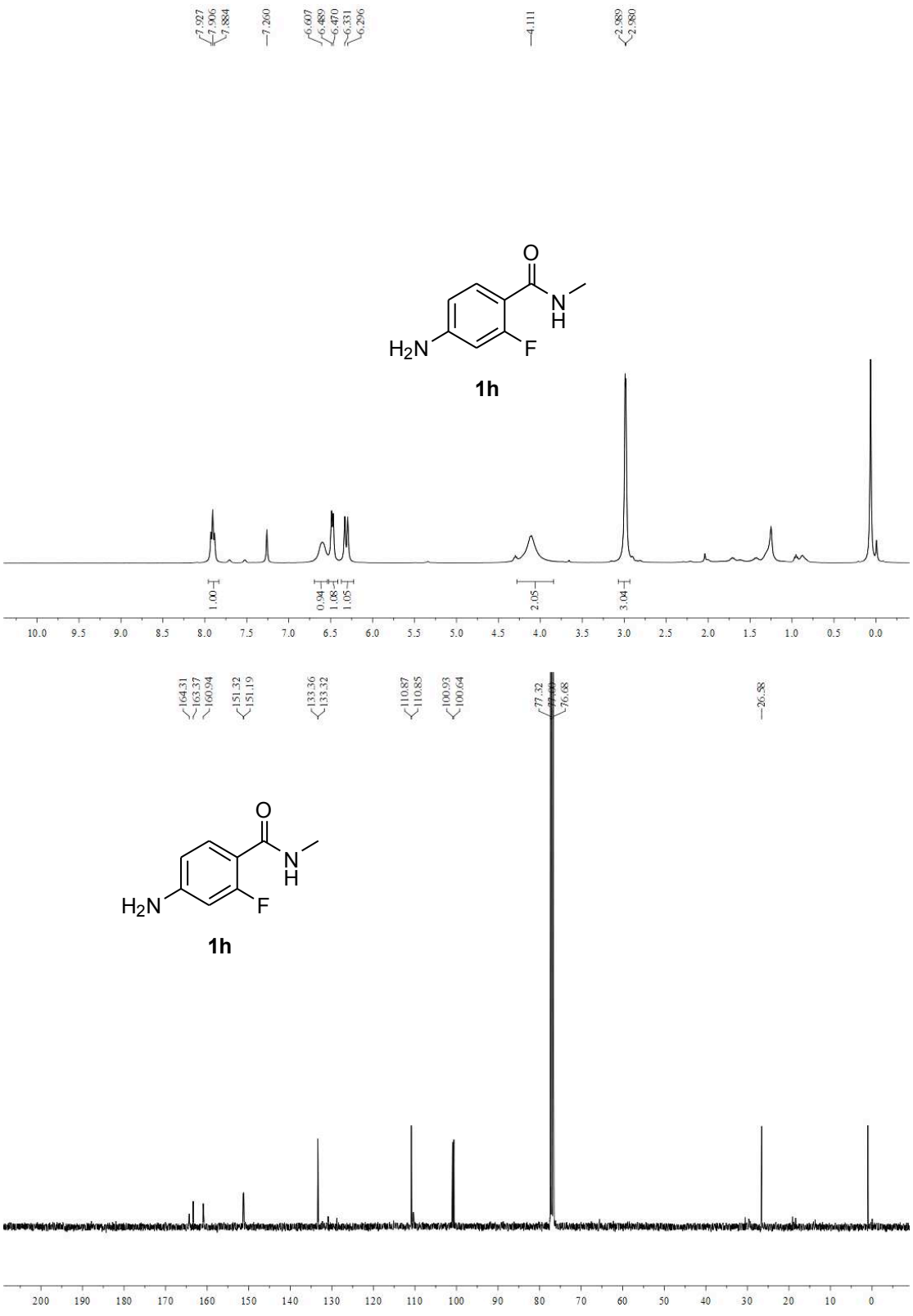
^{19}F NMR spectrum in $CDCl_3$ for compound 1f



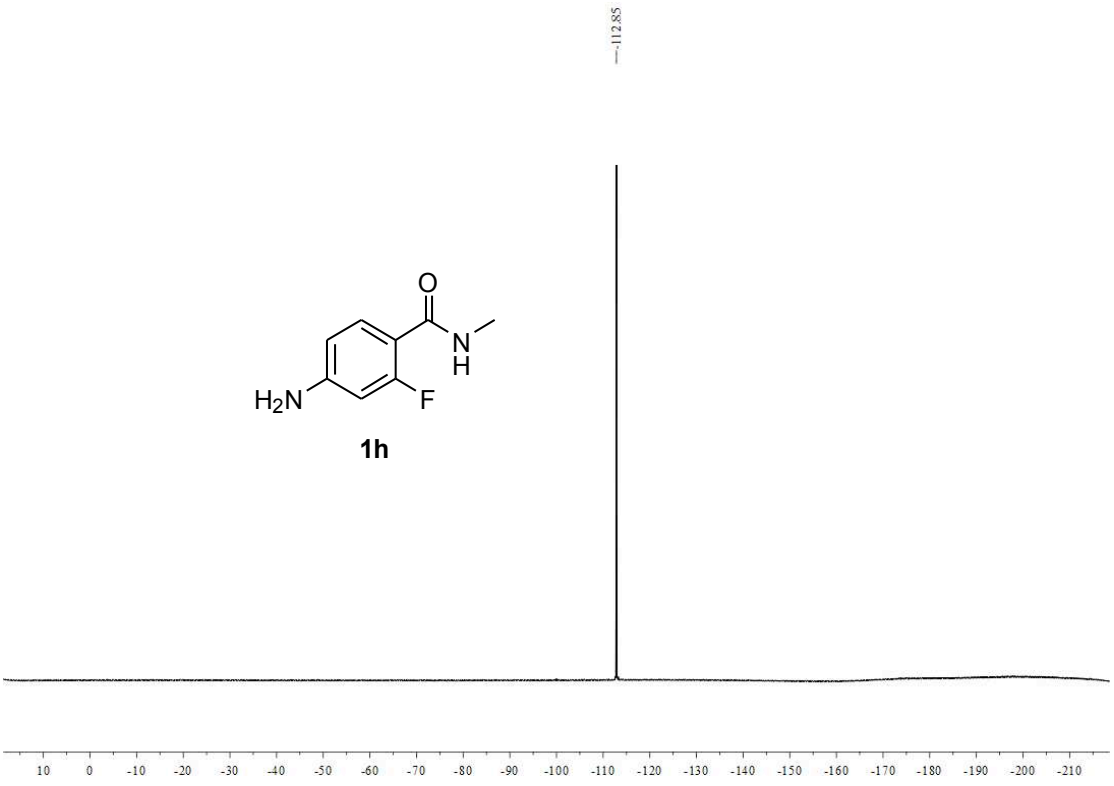
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1g



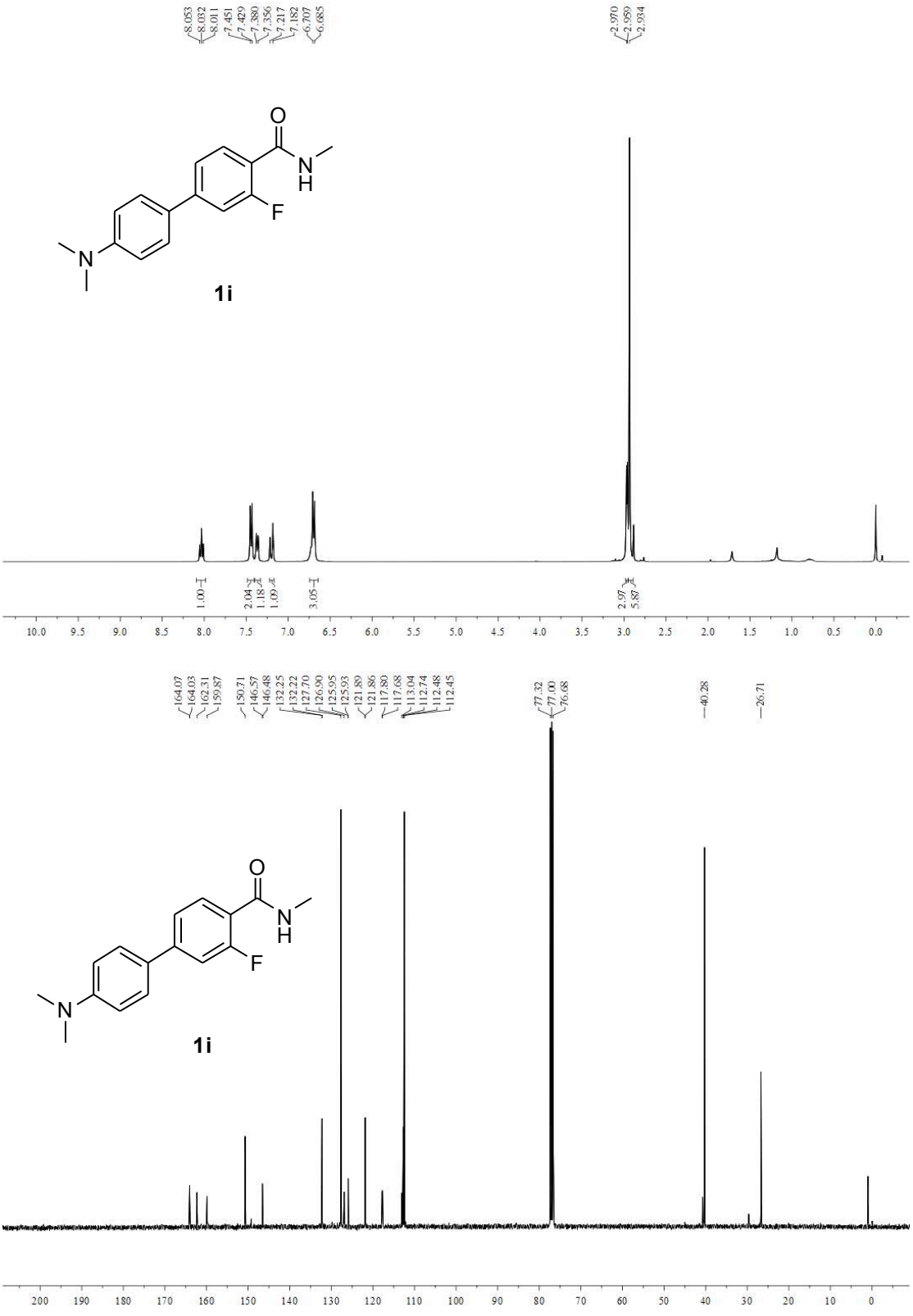
^{19}F NMR spectrum in $CDCl_3$ for compound 1g



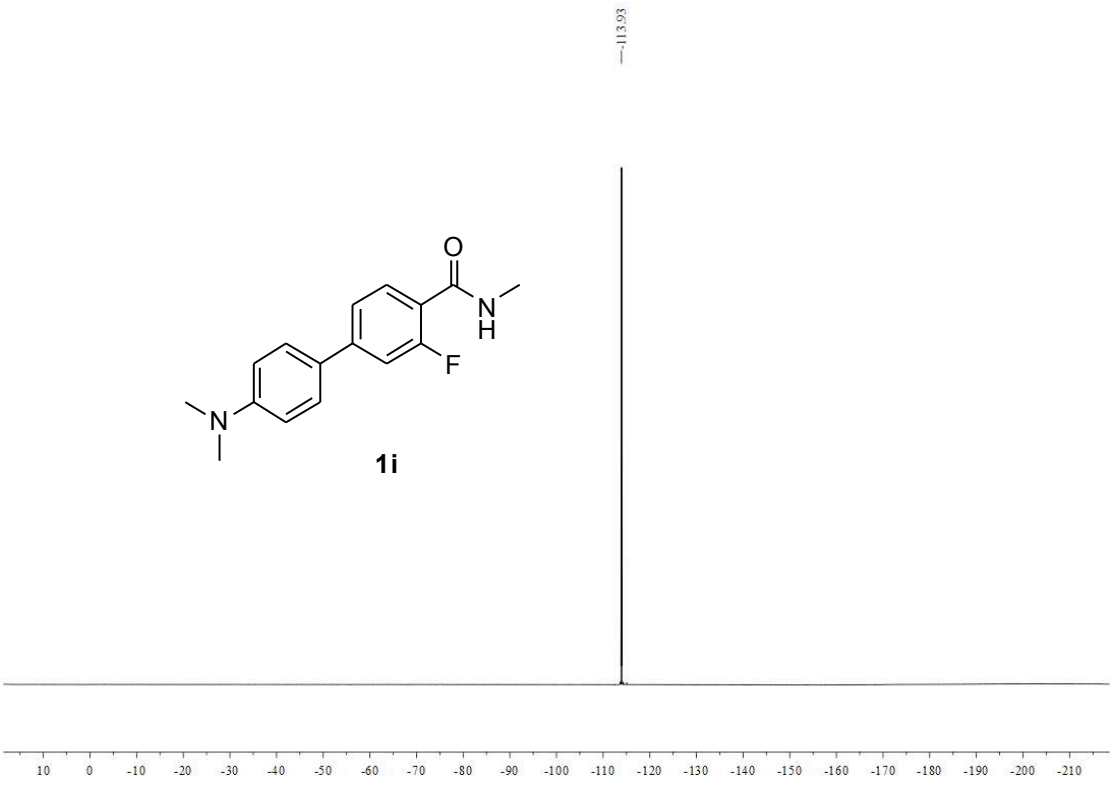
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1h



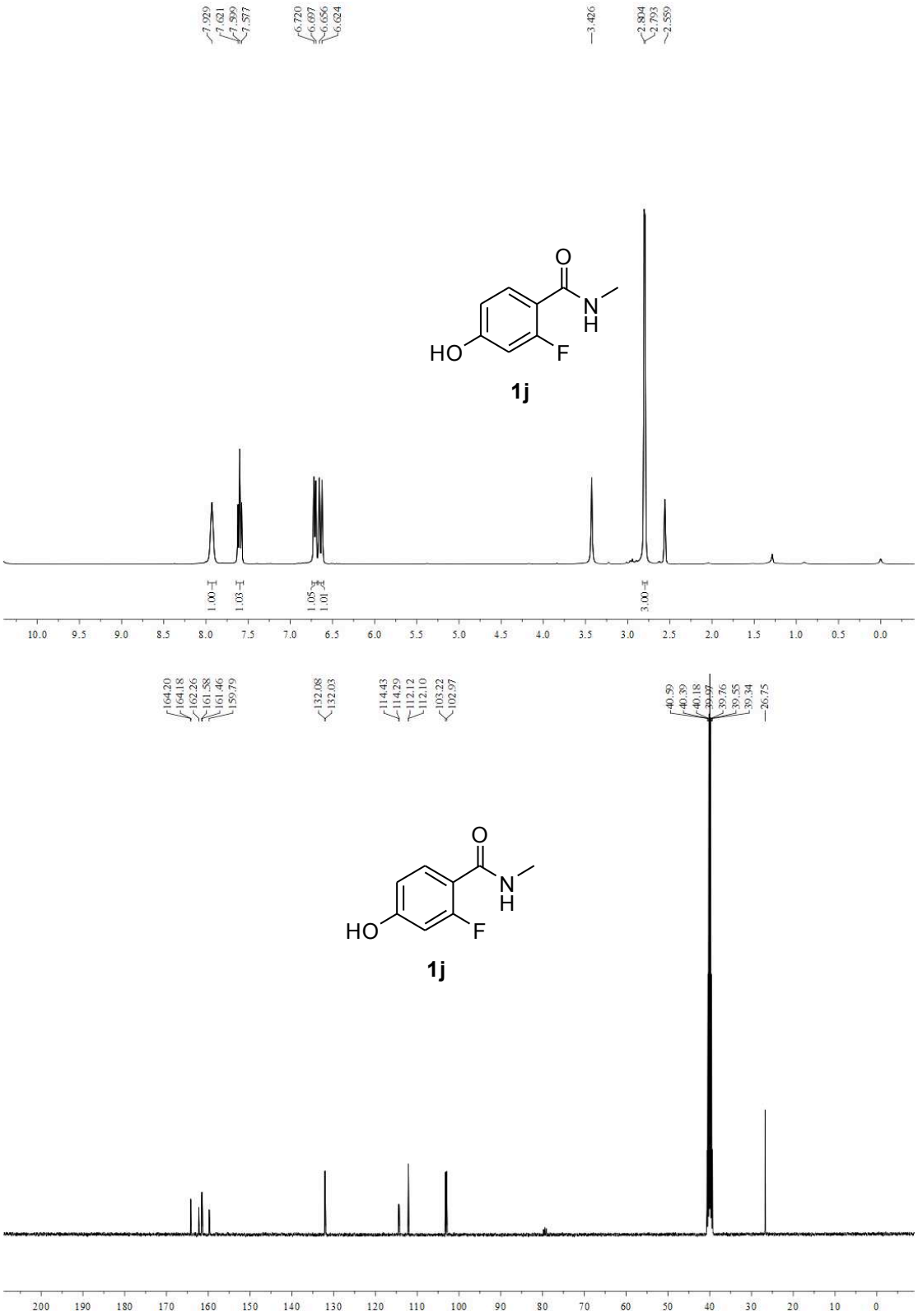
^{19}F NMR spectrum in $CDCl_3$ for compound 1h



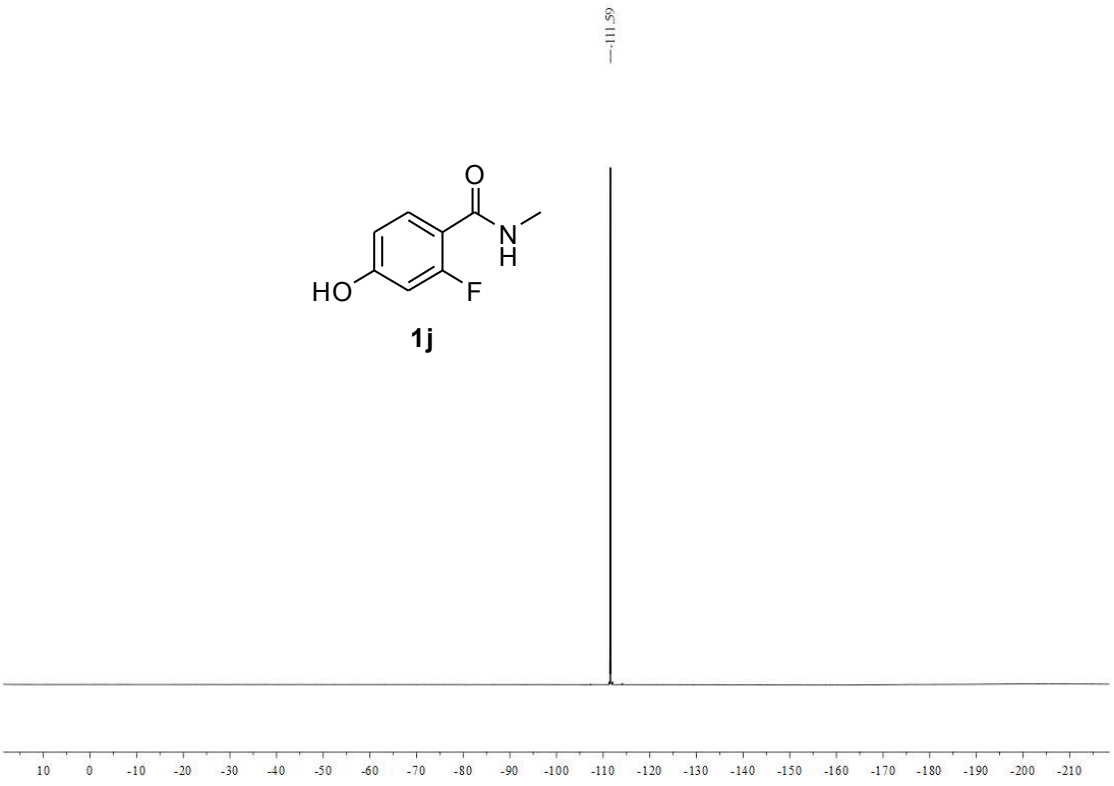
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1i



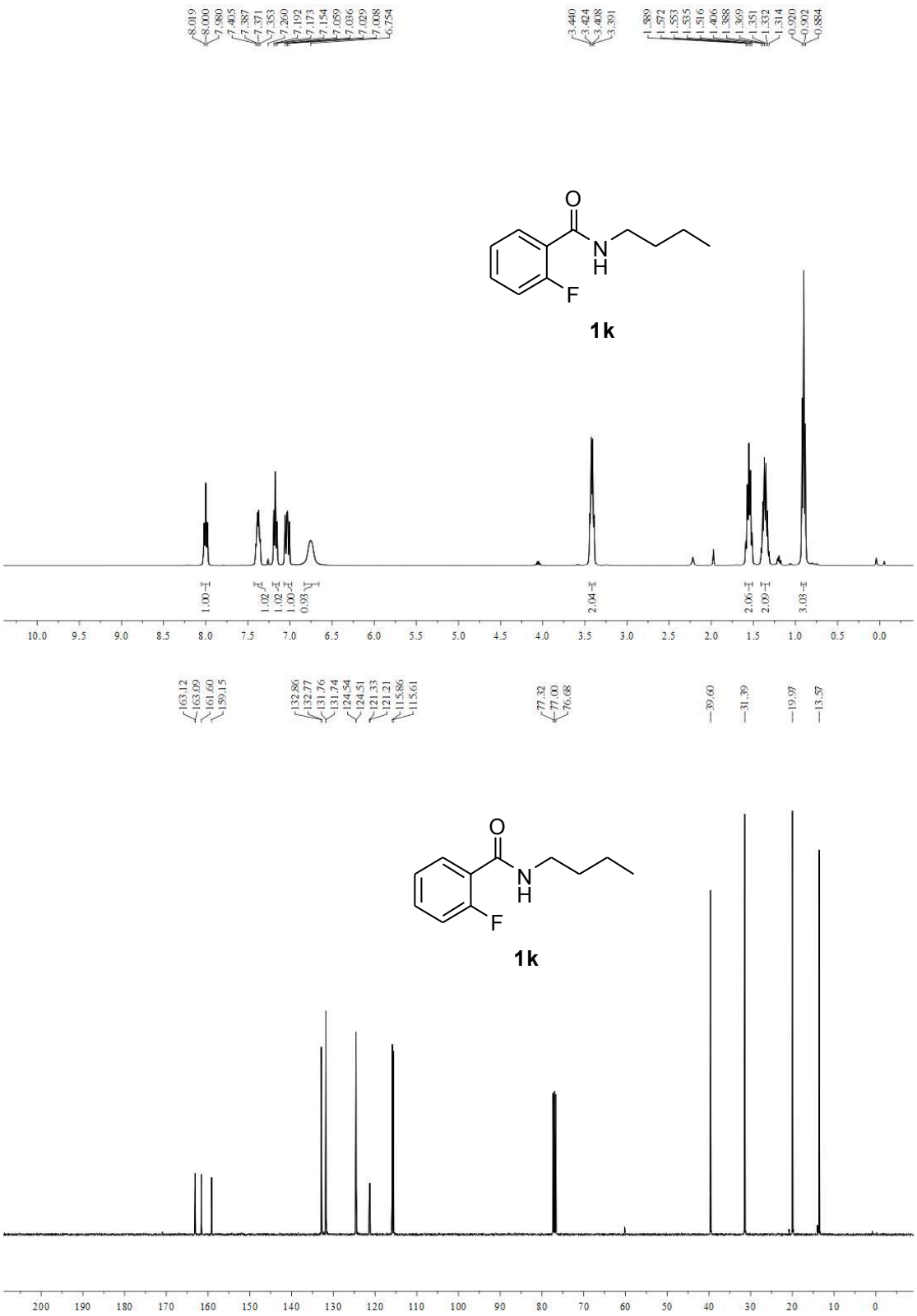
^{19}F NMR spectrum in $CDCl_3$ for compound 1i



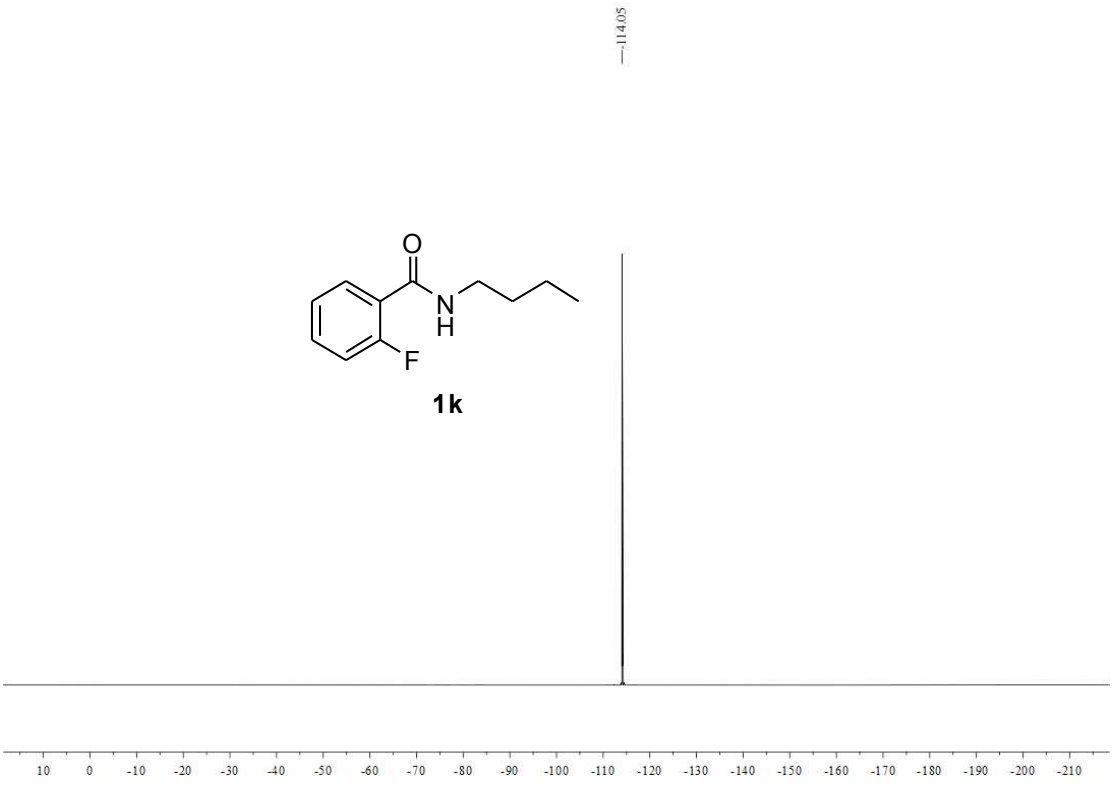
^{1}H and ^{13}C NMR spectra in DMSO-d_6 for compound 1j



^{19}F NMR spectrum in DMSO-d_6 for compound 1j

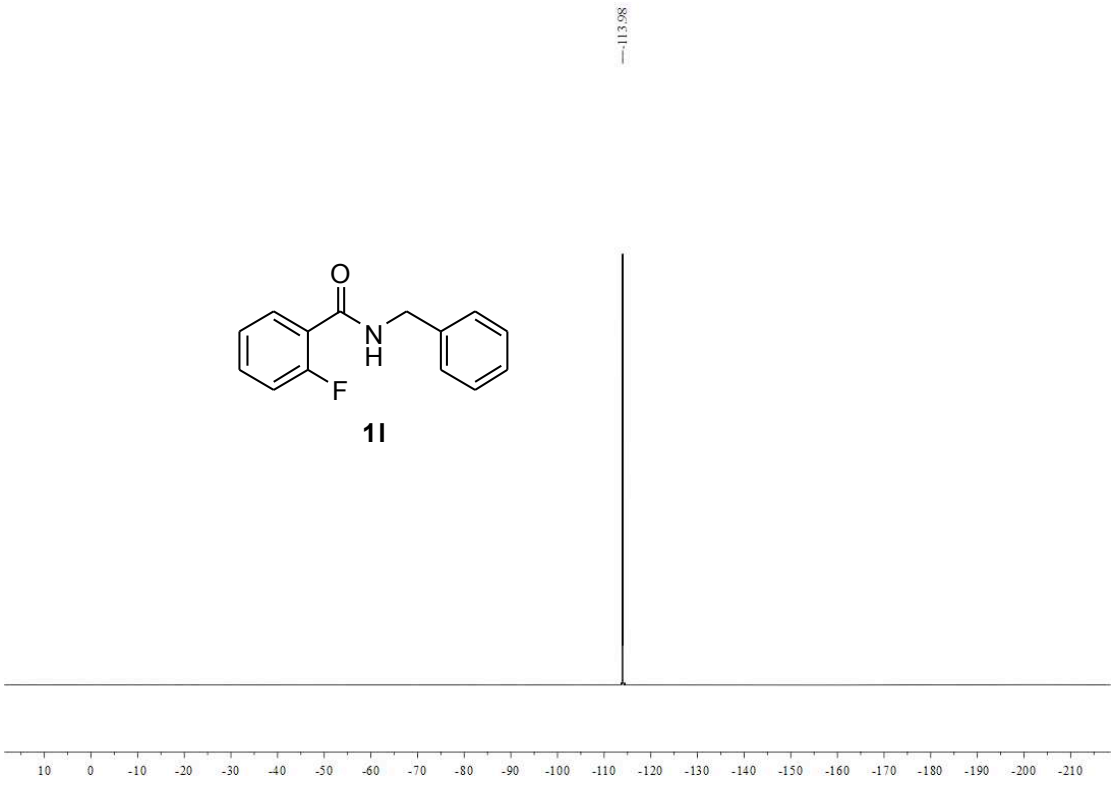


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1k



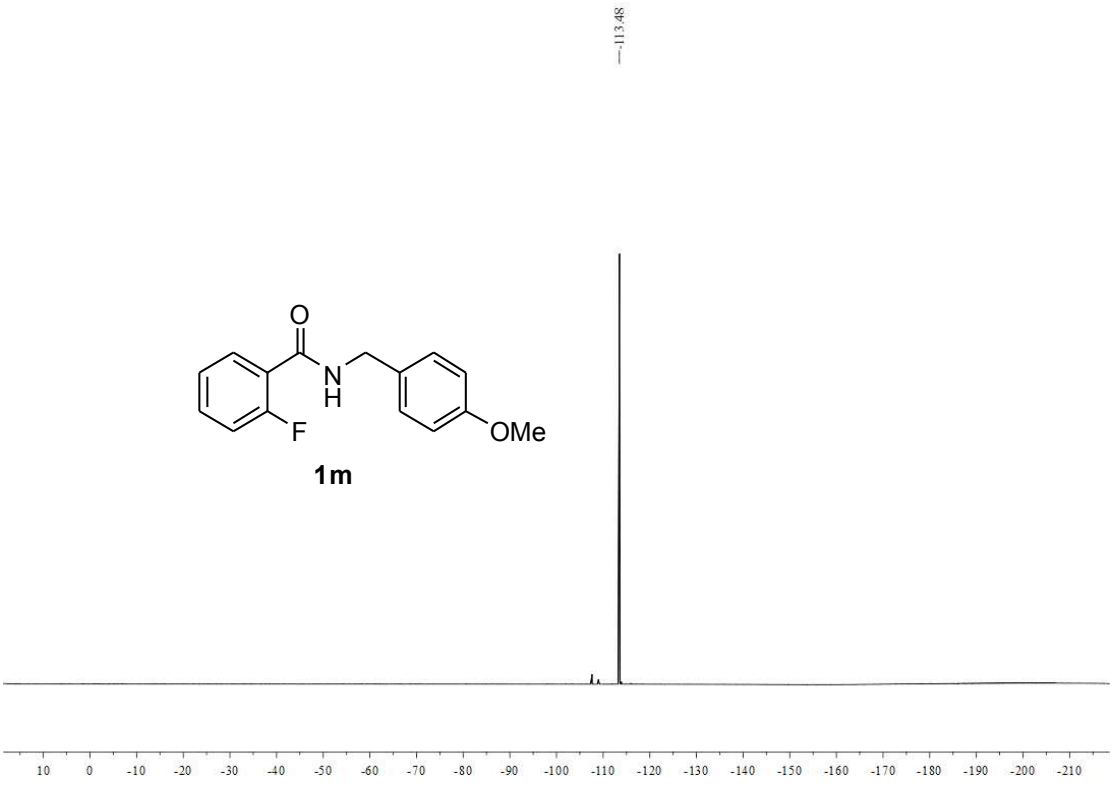
^{19}F NMR spectrum in $CDCl_3$ for compound 1k

^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1l

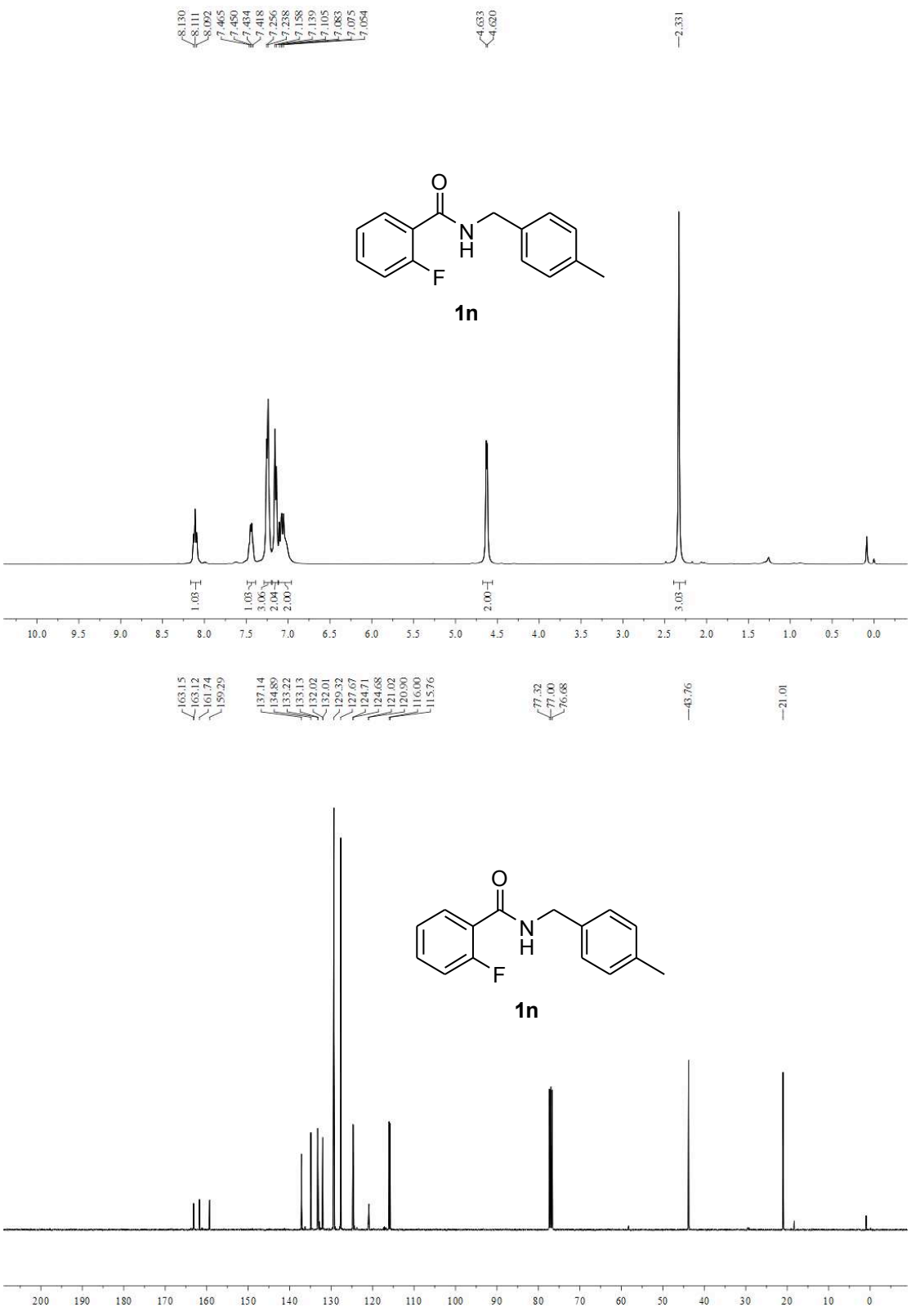


^{19}F NMR spectrum in $CDCl_3$ for compound 1l

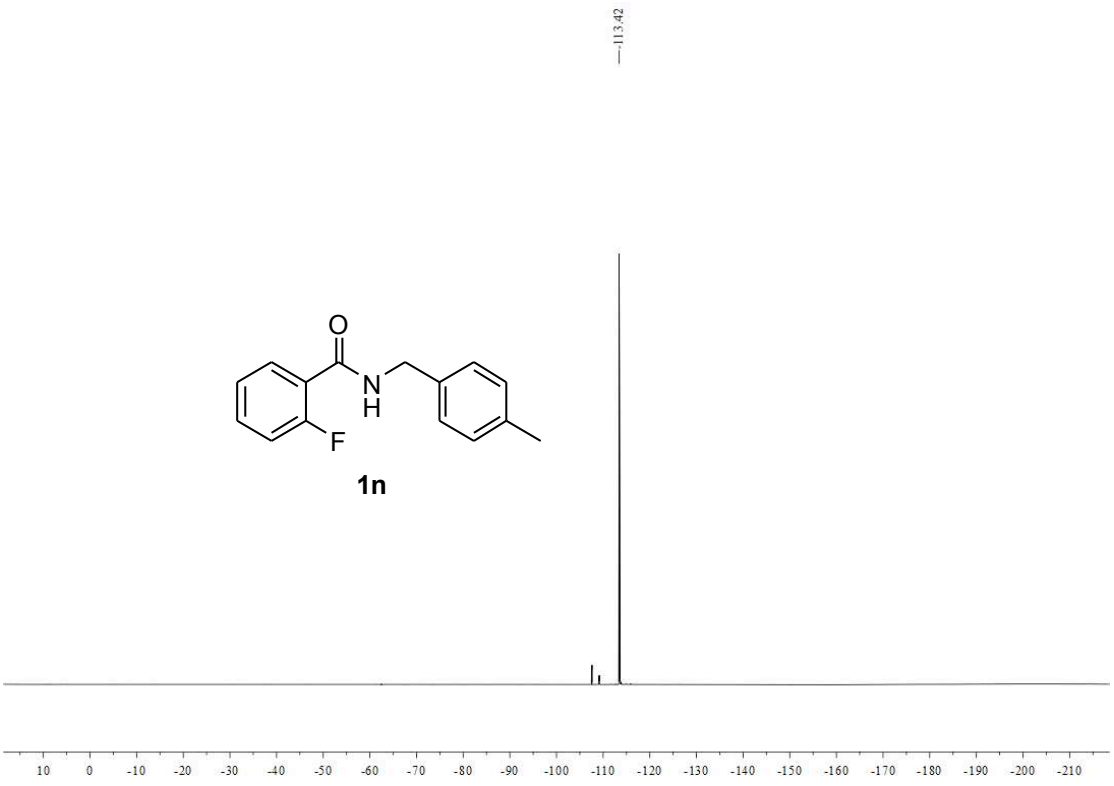
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1m



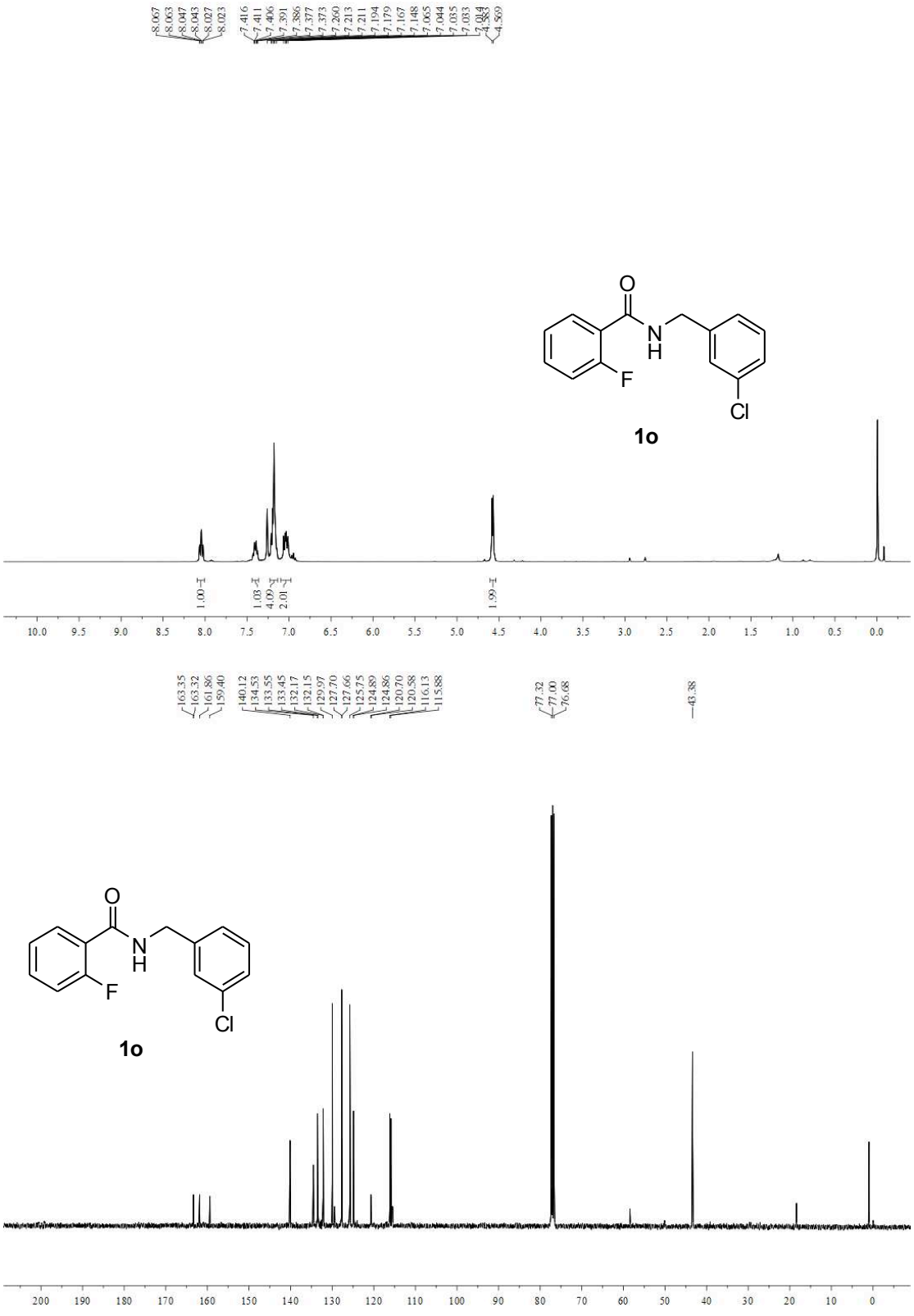
^{19}F NMR spectrum in $CDCl_3$ for compound 1m



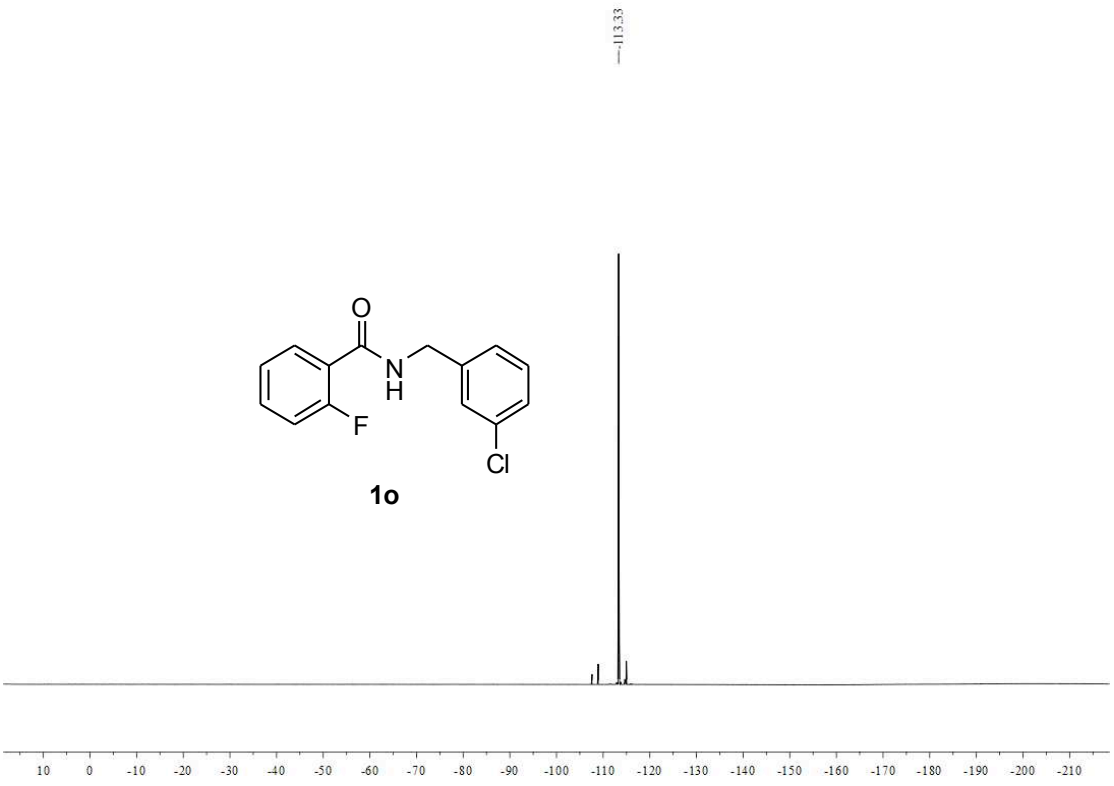
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1n



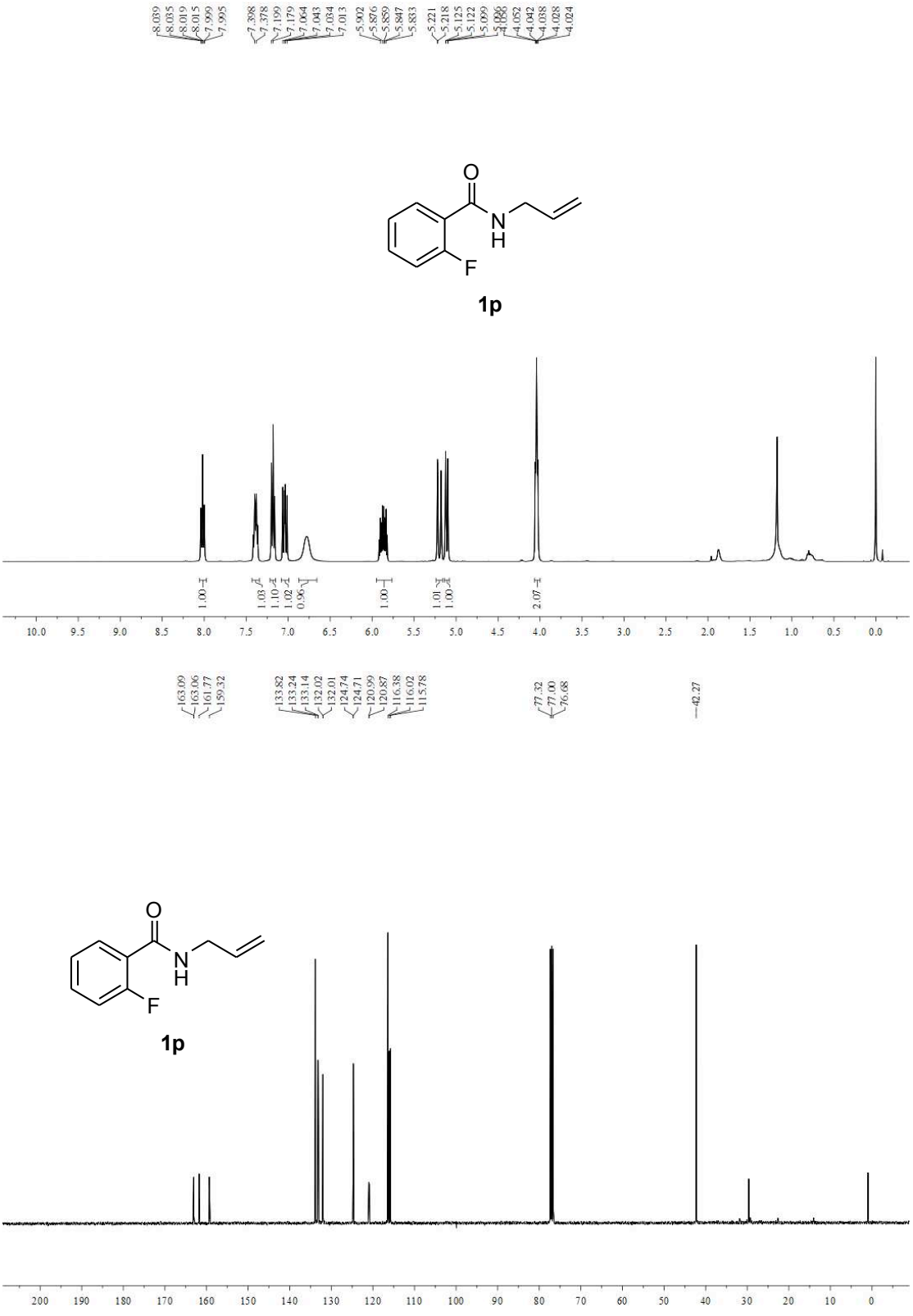
^{19}F NMR spectrum in $CDCl_3$ for compound 1n



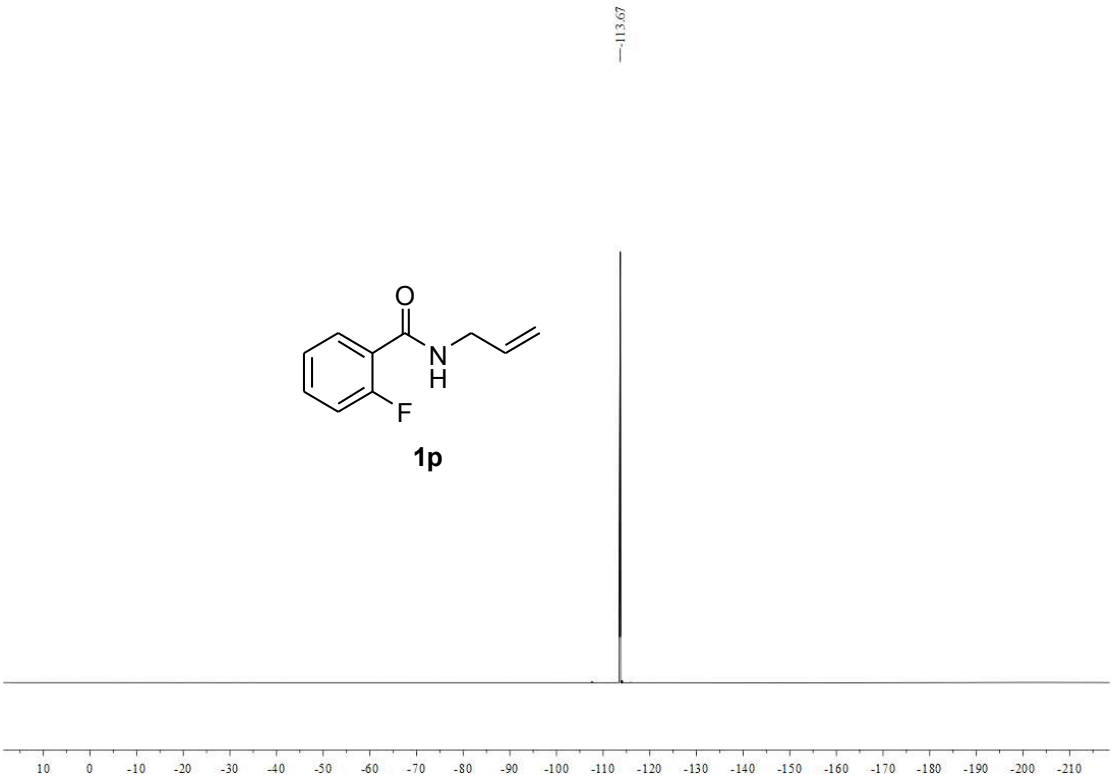
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1o



^{19}F NMR spectrum in $CDCl_3$ for compound 1o

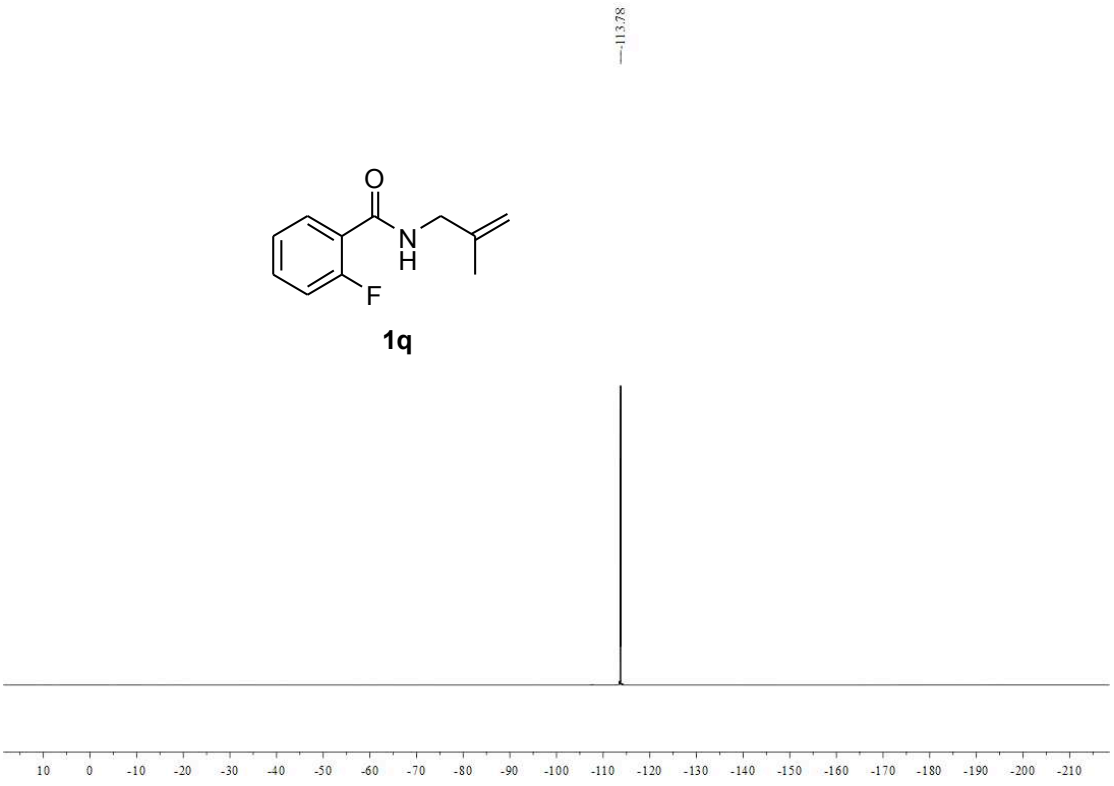


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1p

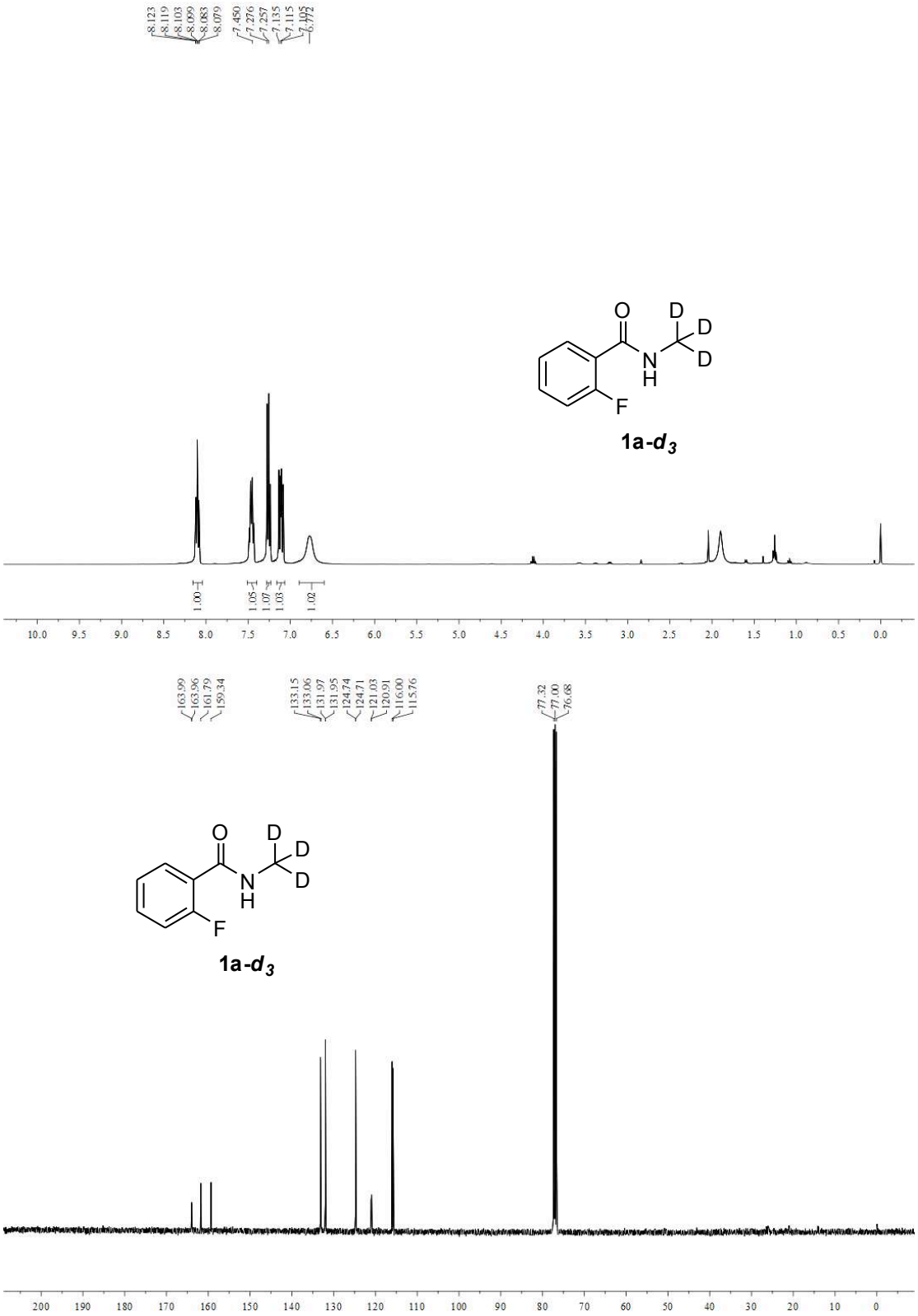


^{19}F NMR spectrum in $CDCl_3$ for compound 1p

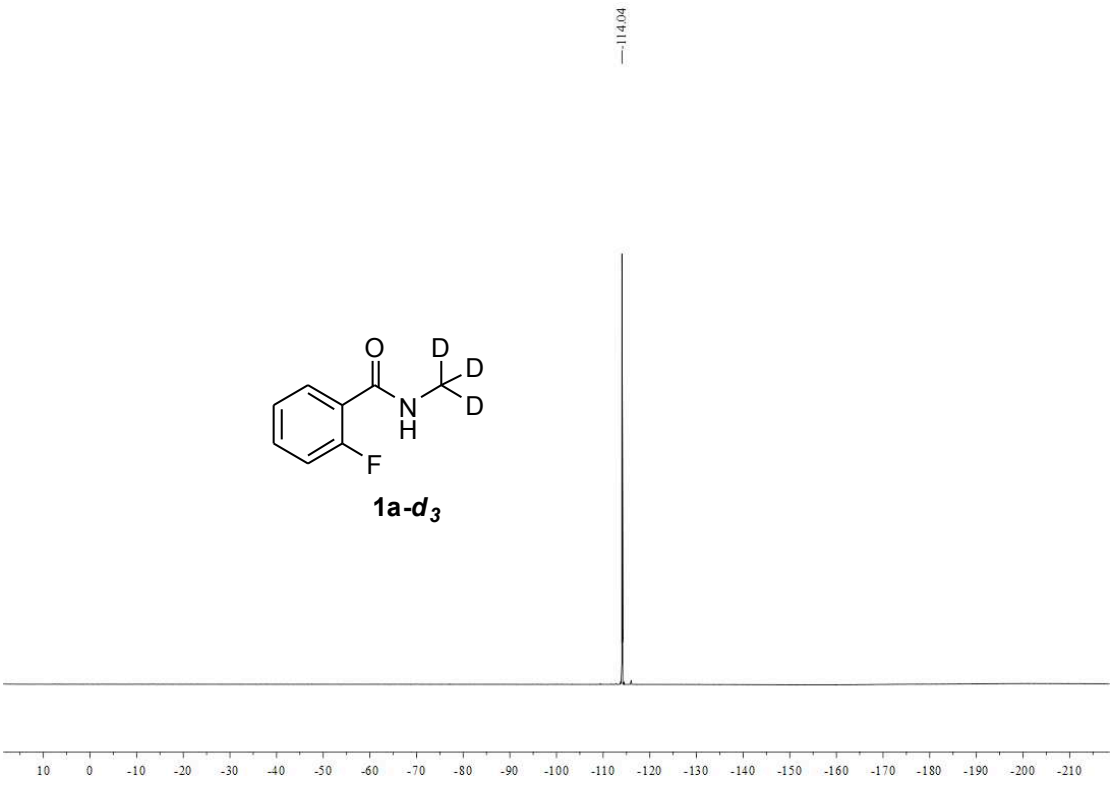
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1q



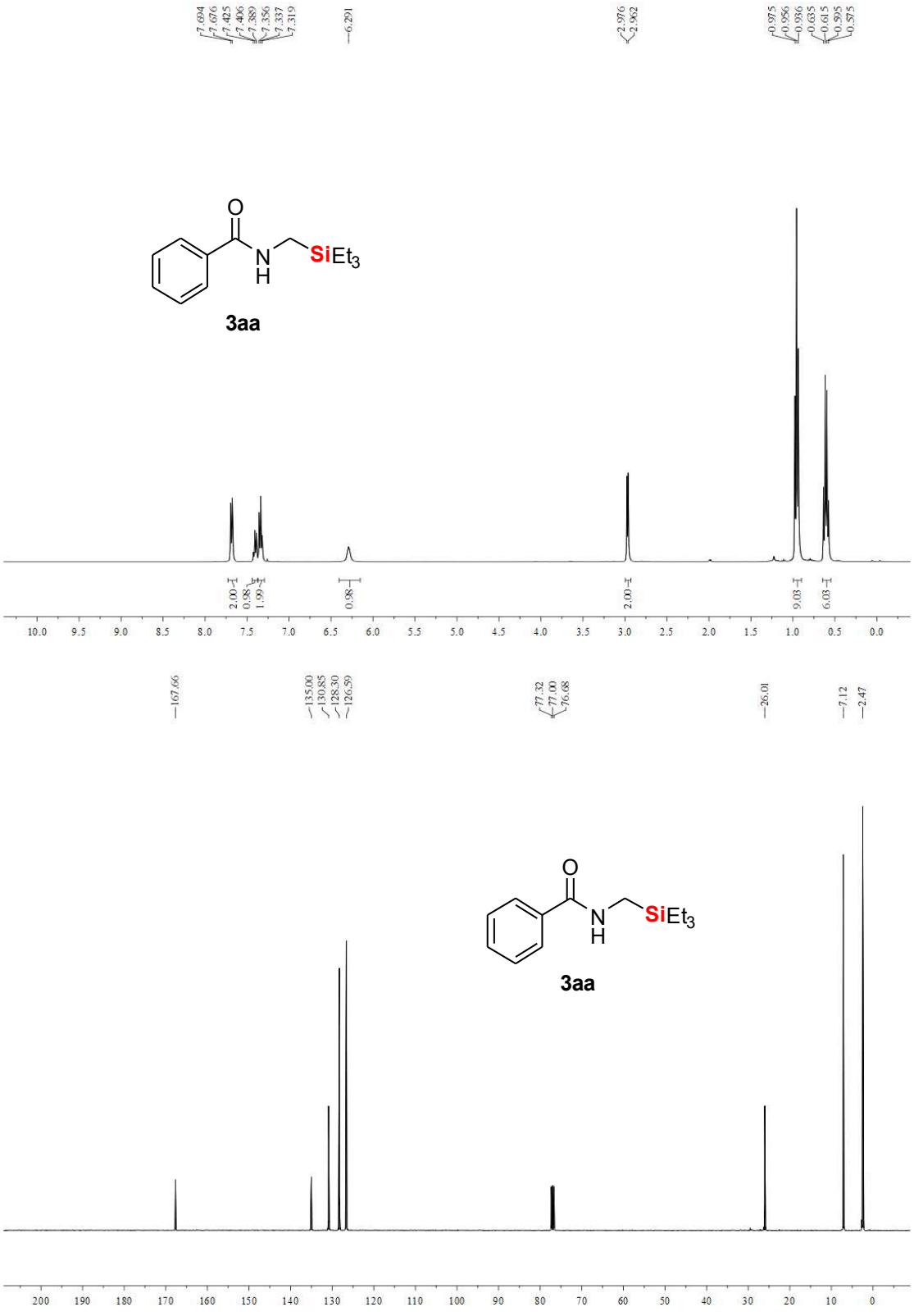
^{19}F NMR spectrum in $CDCl_3$ for compound 1aq



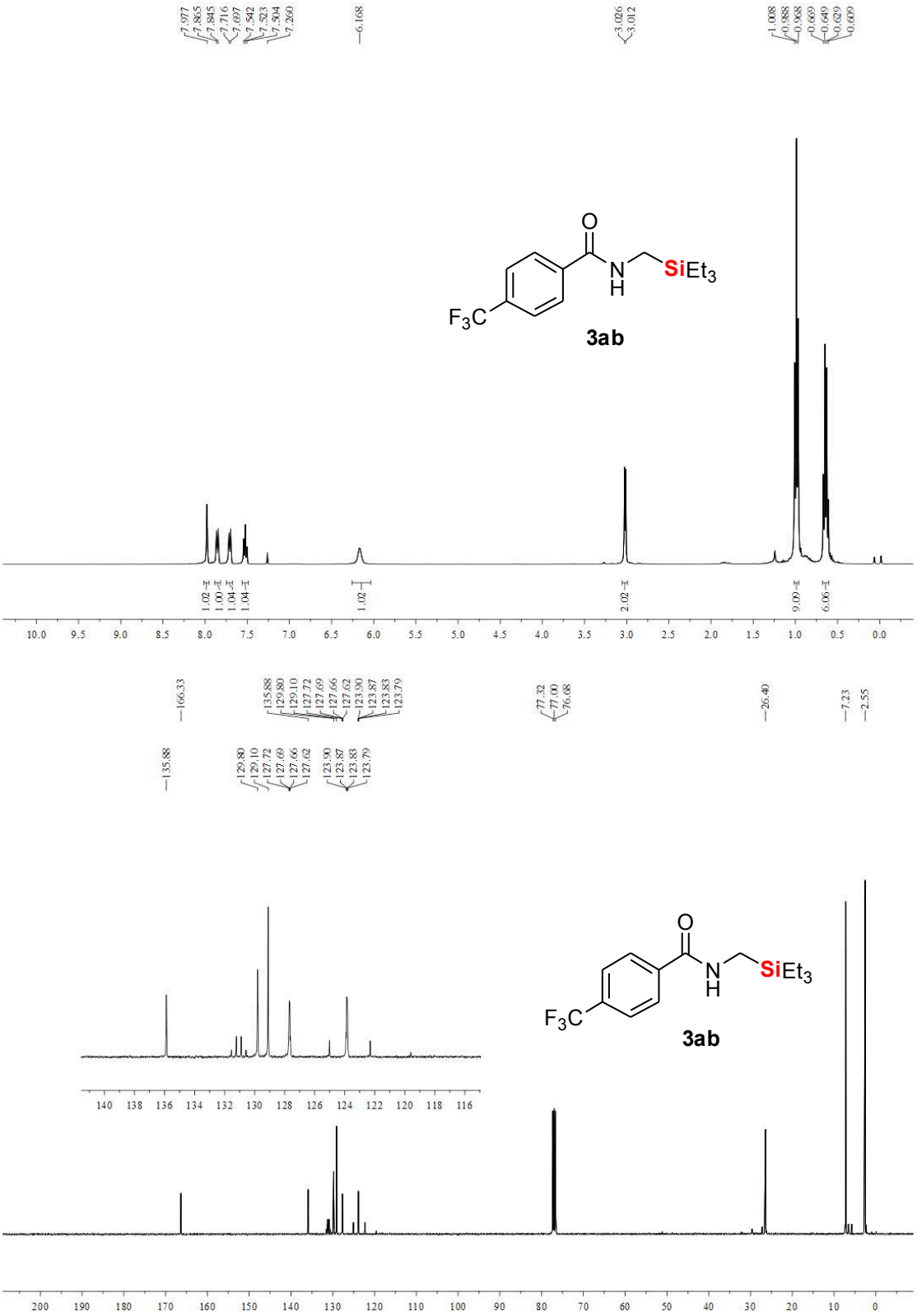
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1a-*d*$_3$



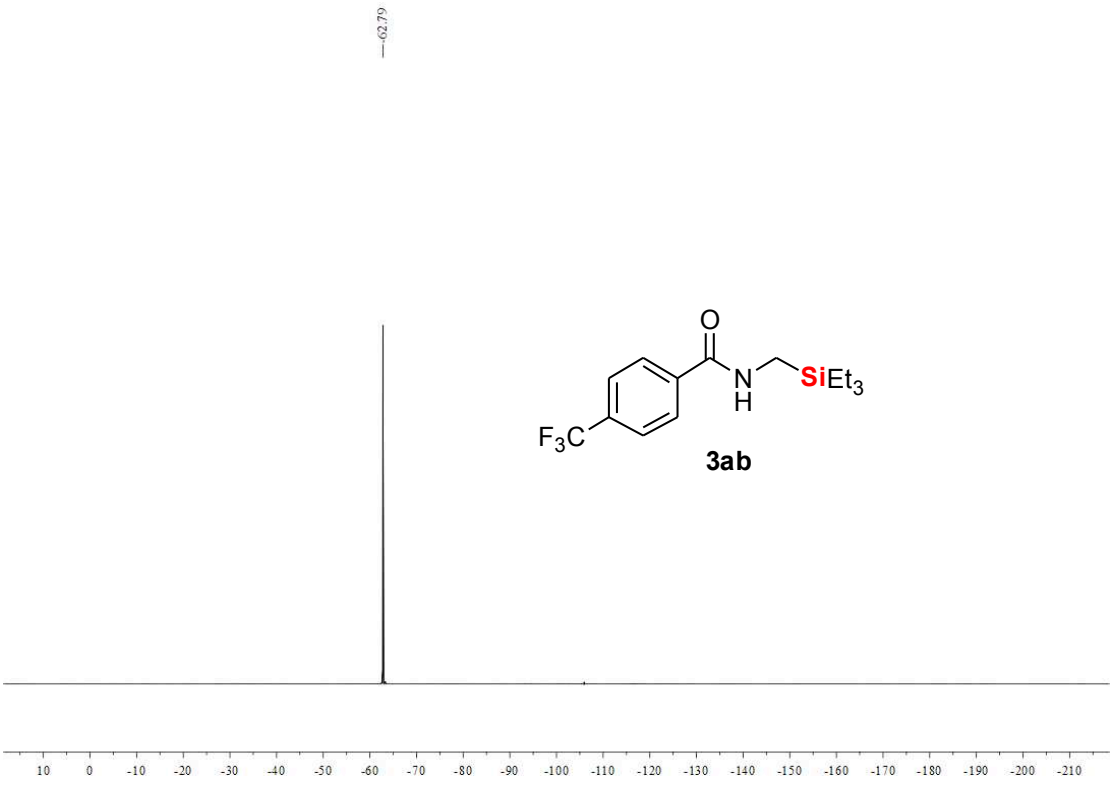
^{19}F NMR spectrum in $CDCl_3$ for compound 1a-*d*$_3$



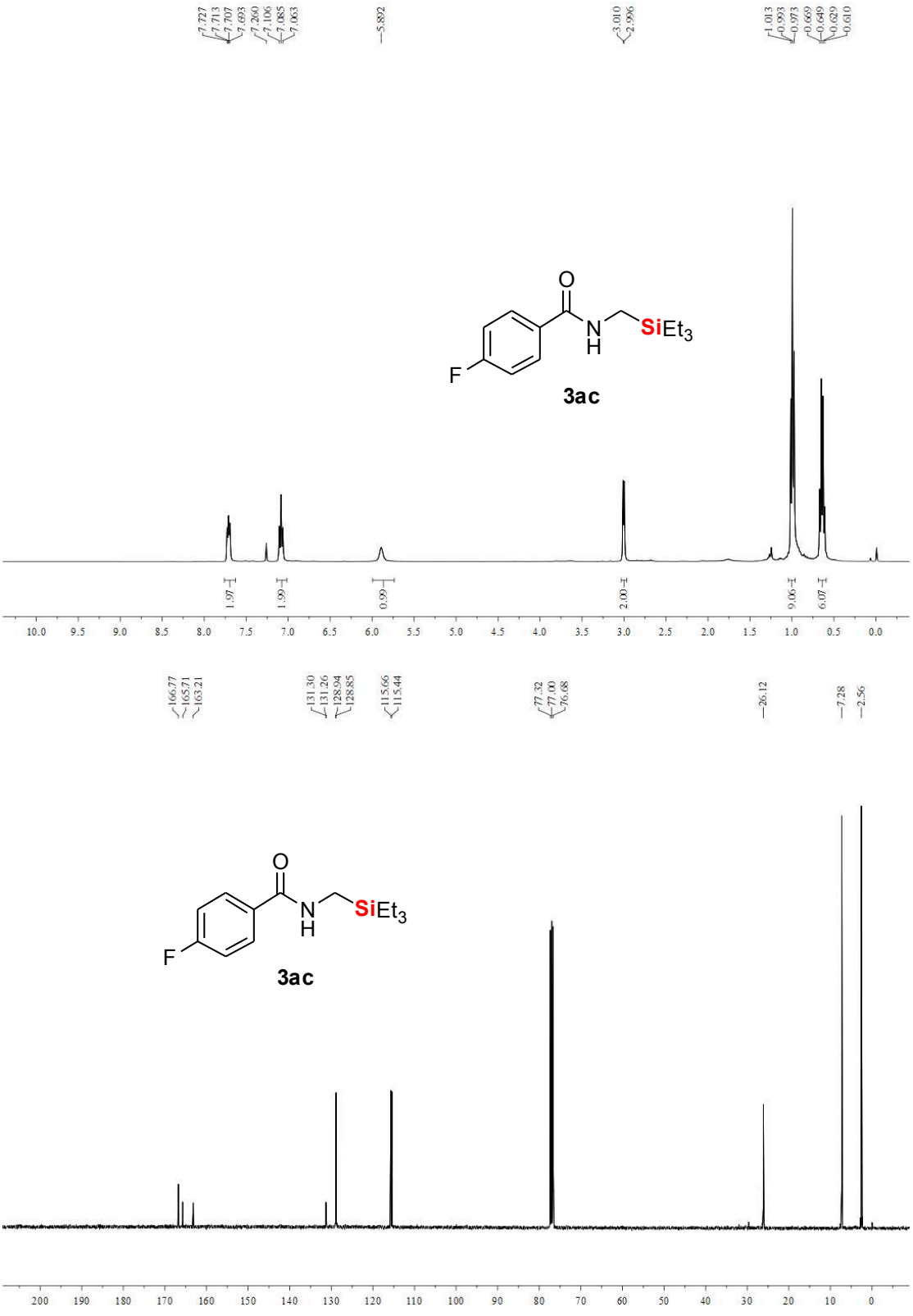
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3aa



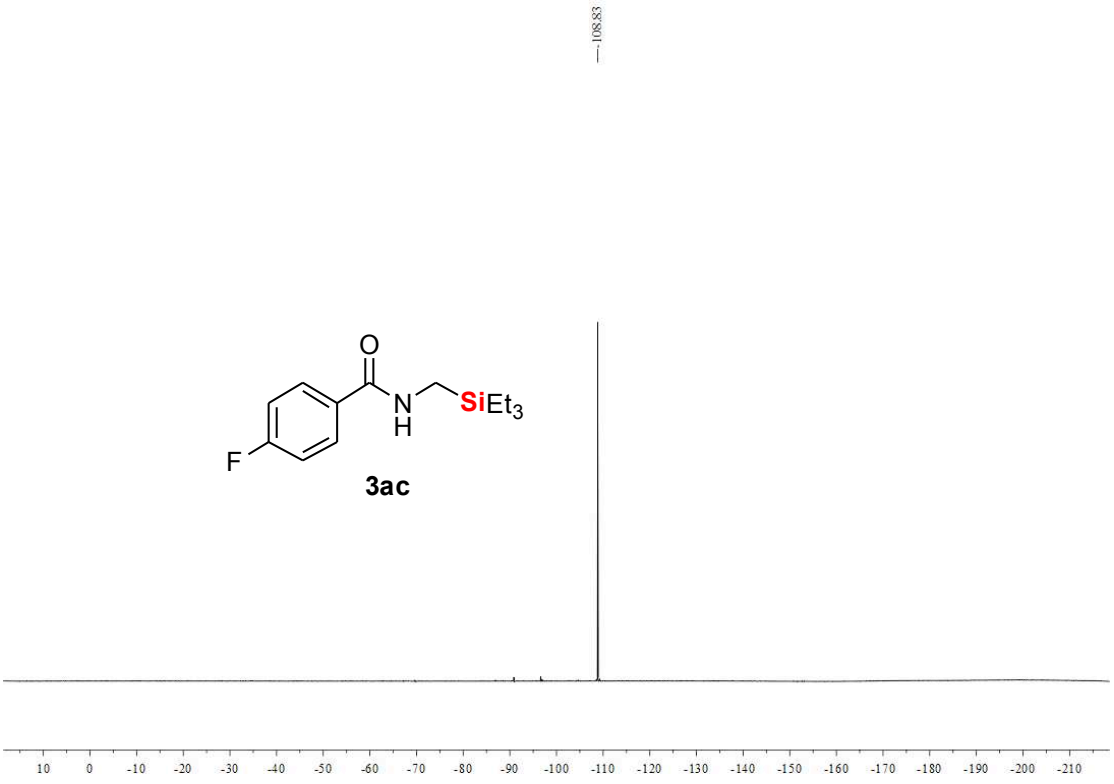
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ab



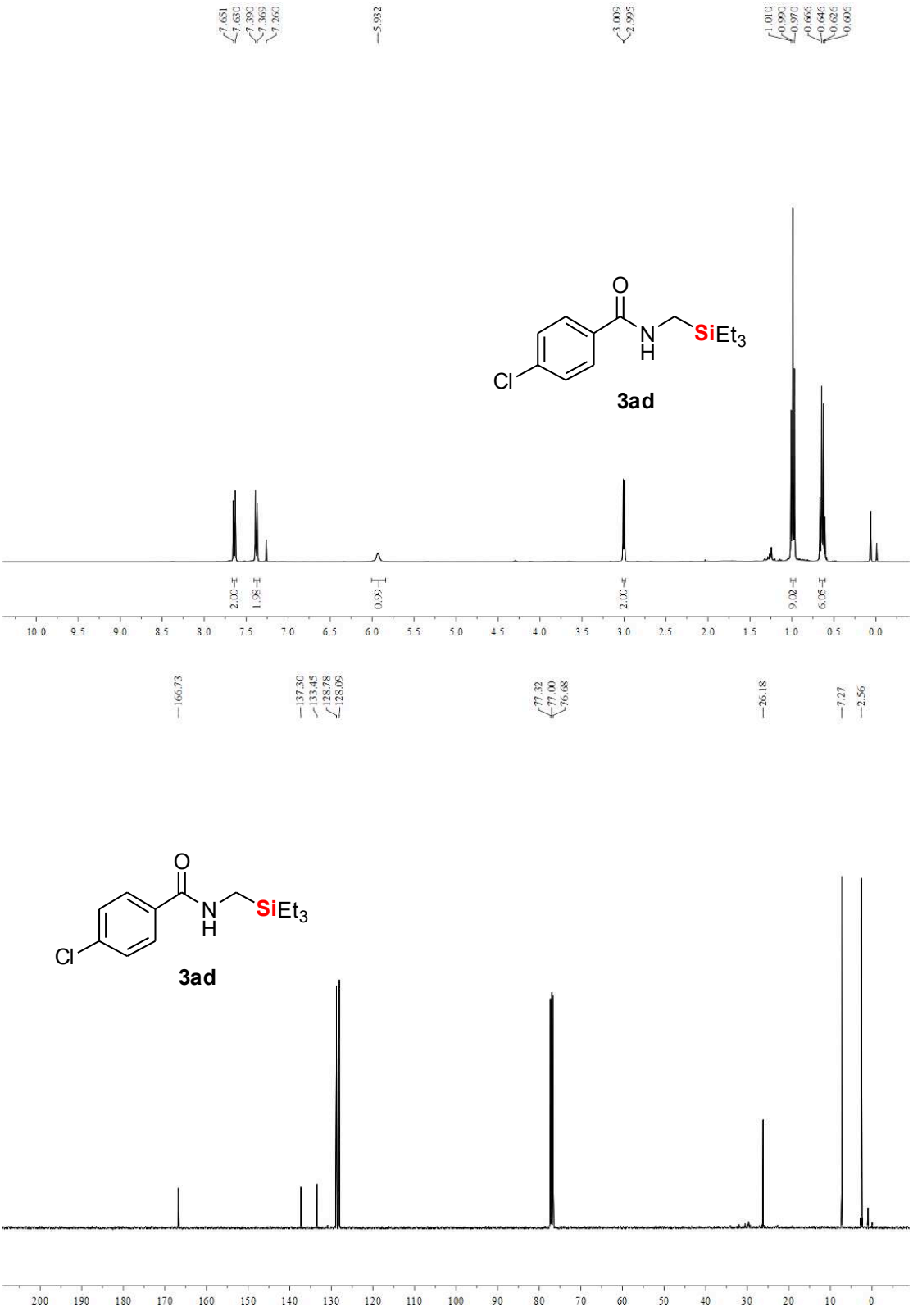
^{19}F NMR spectrum in $CDCl_3$ for compound 3ab



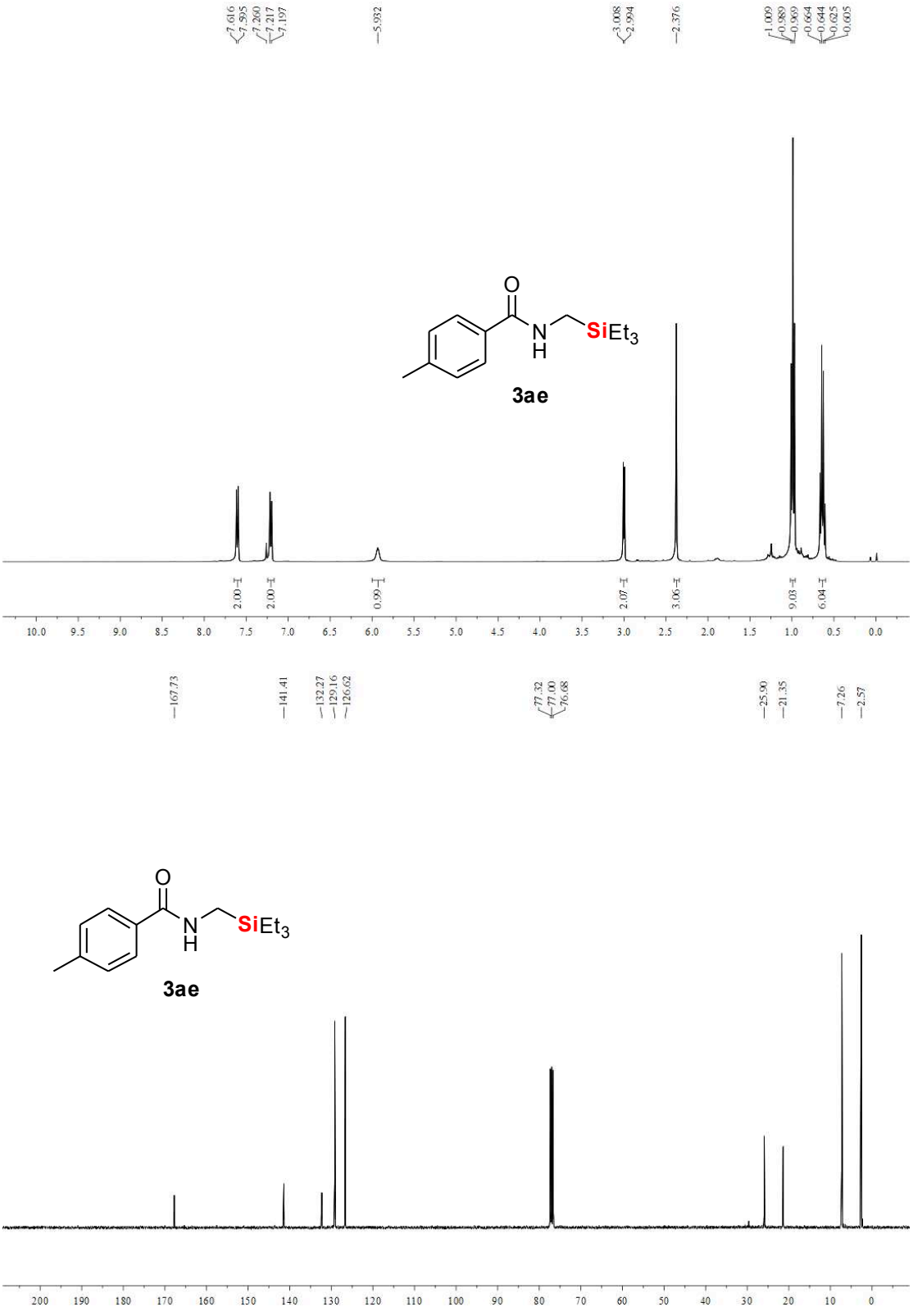
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ac



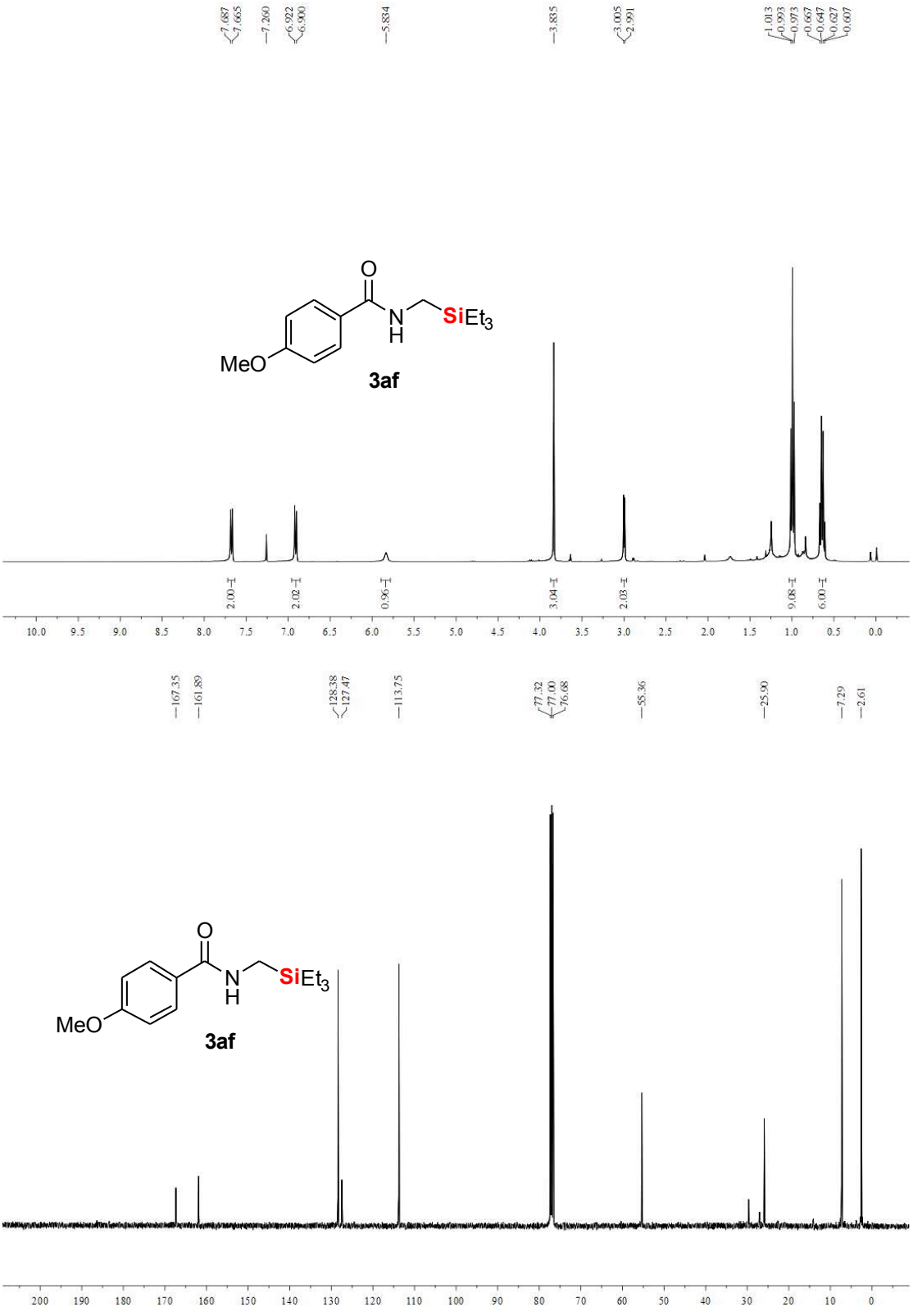
^{19}F NMR spectrum in $CDCl_3$ for compound 3ac



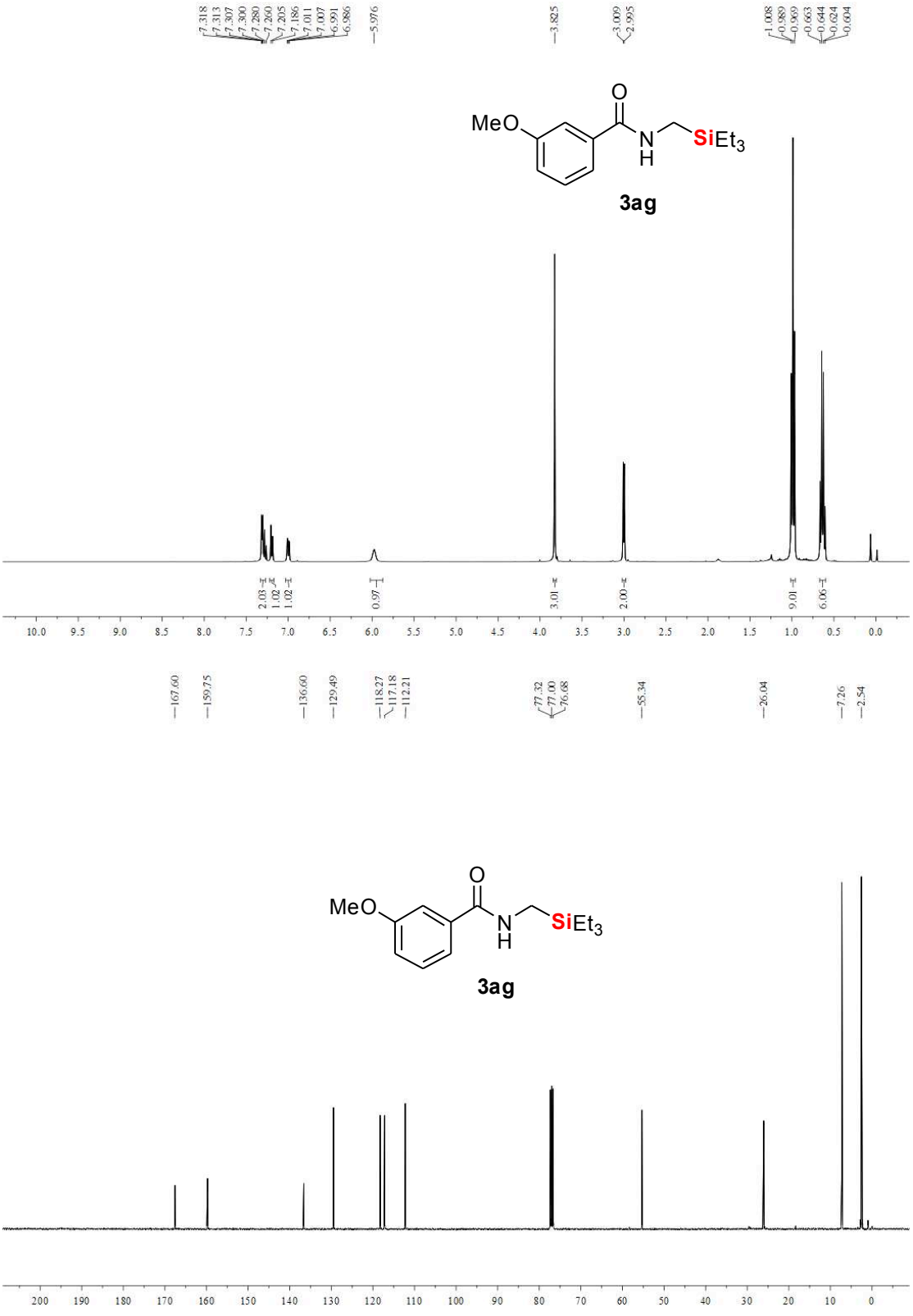
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ad



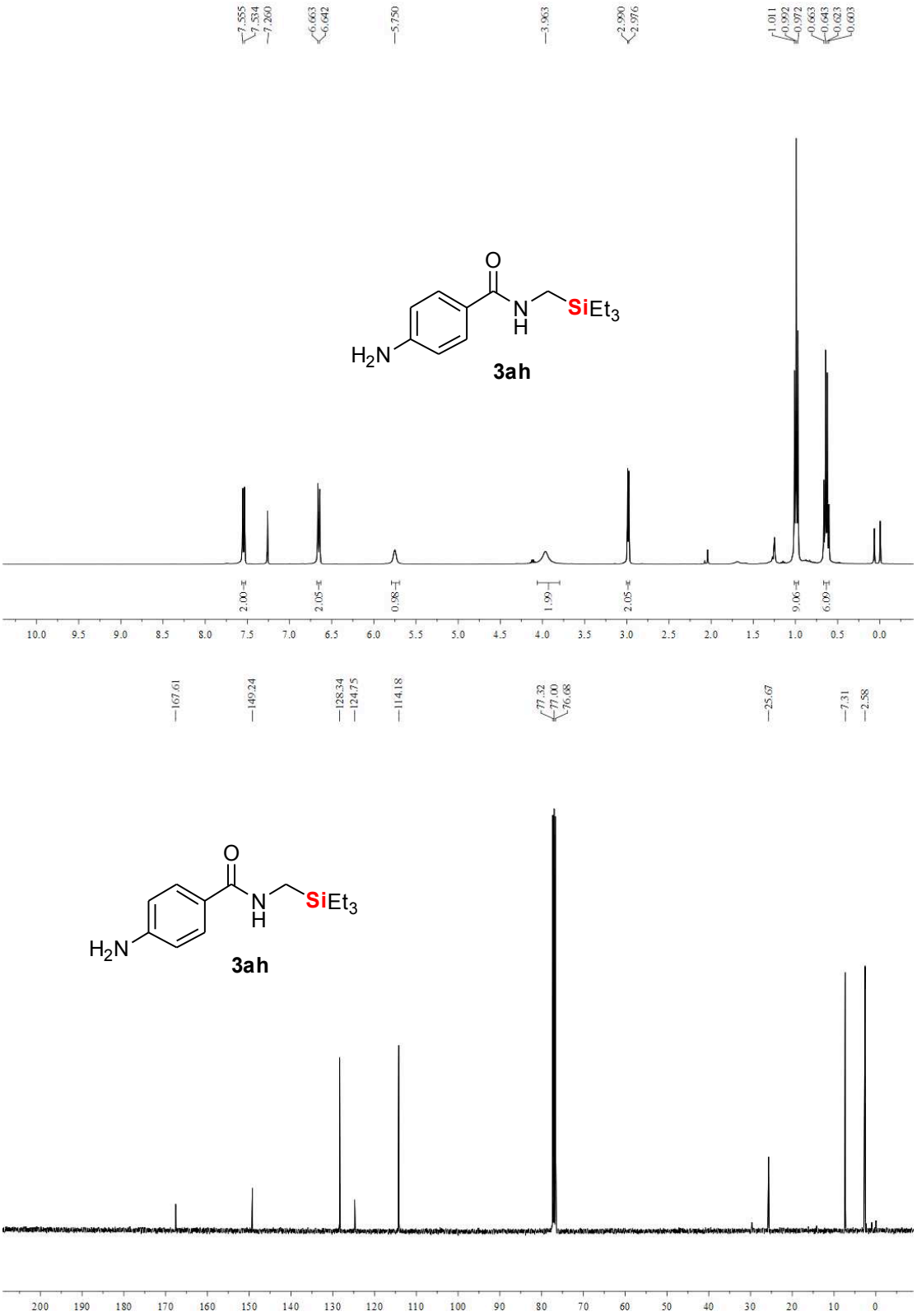
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ae



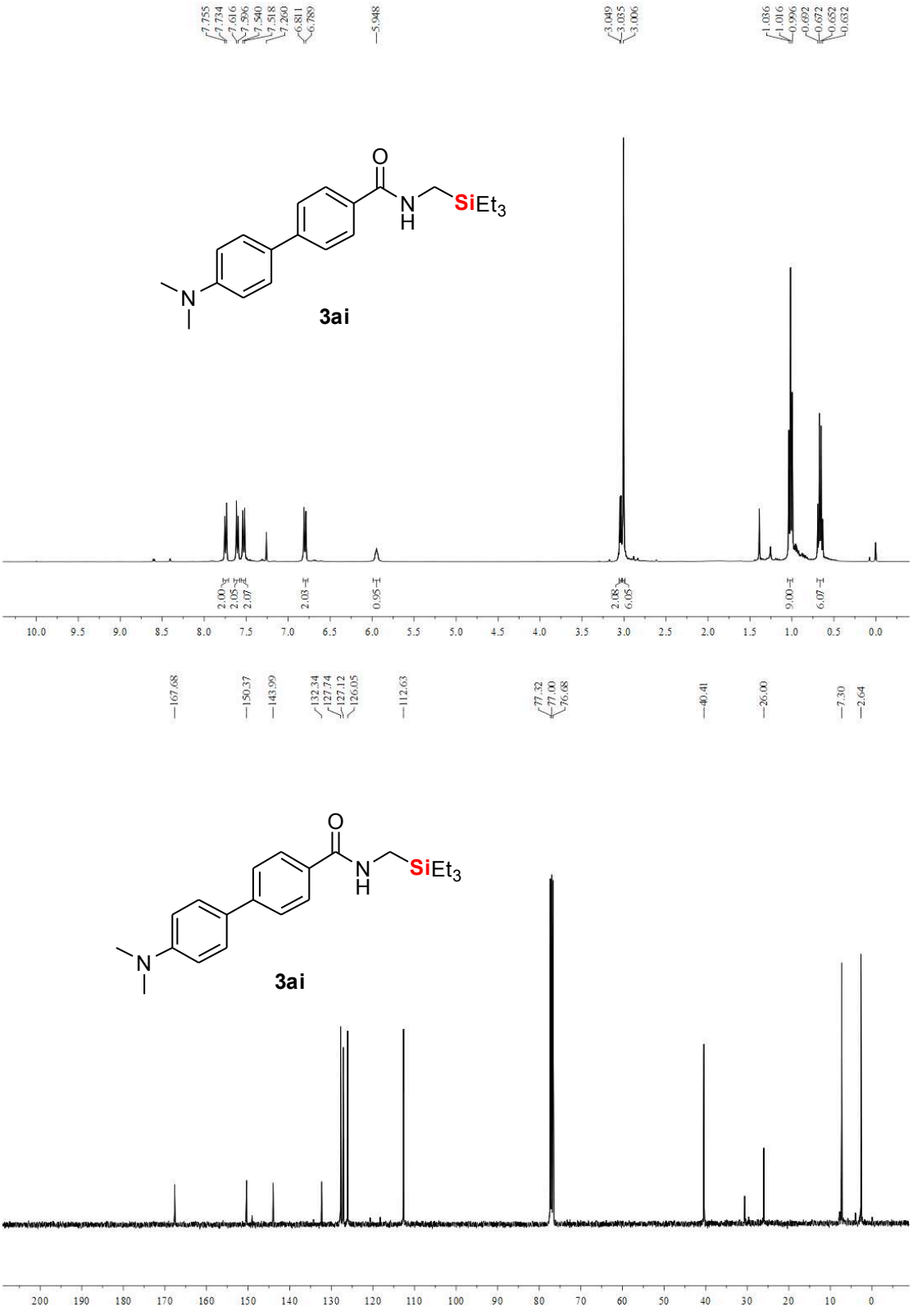
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3af



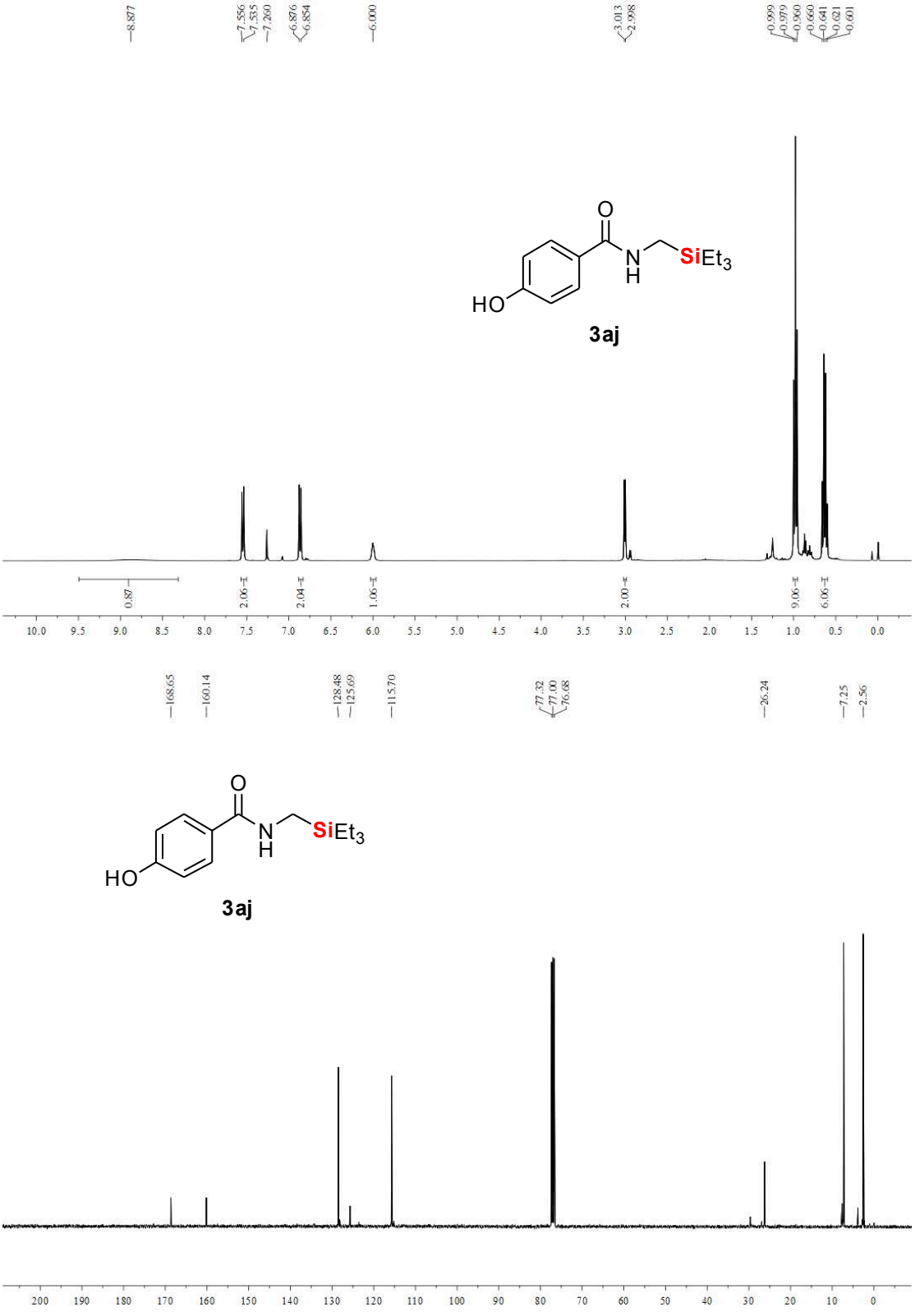
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ag



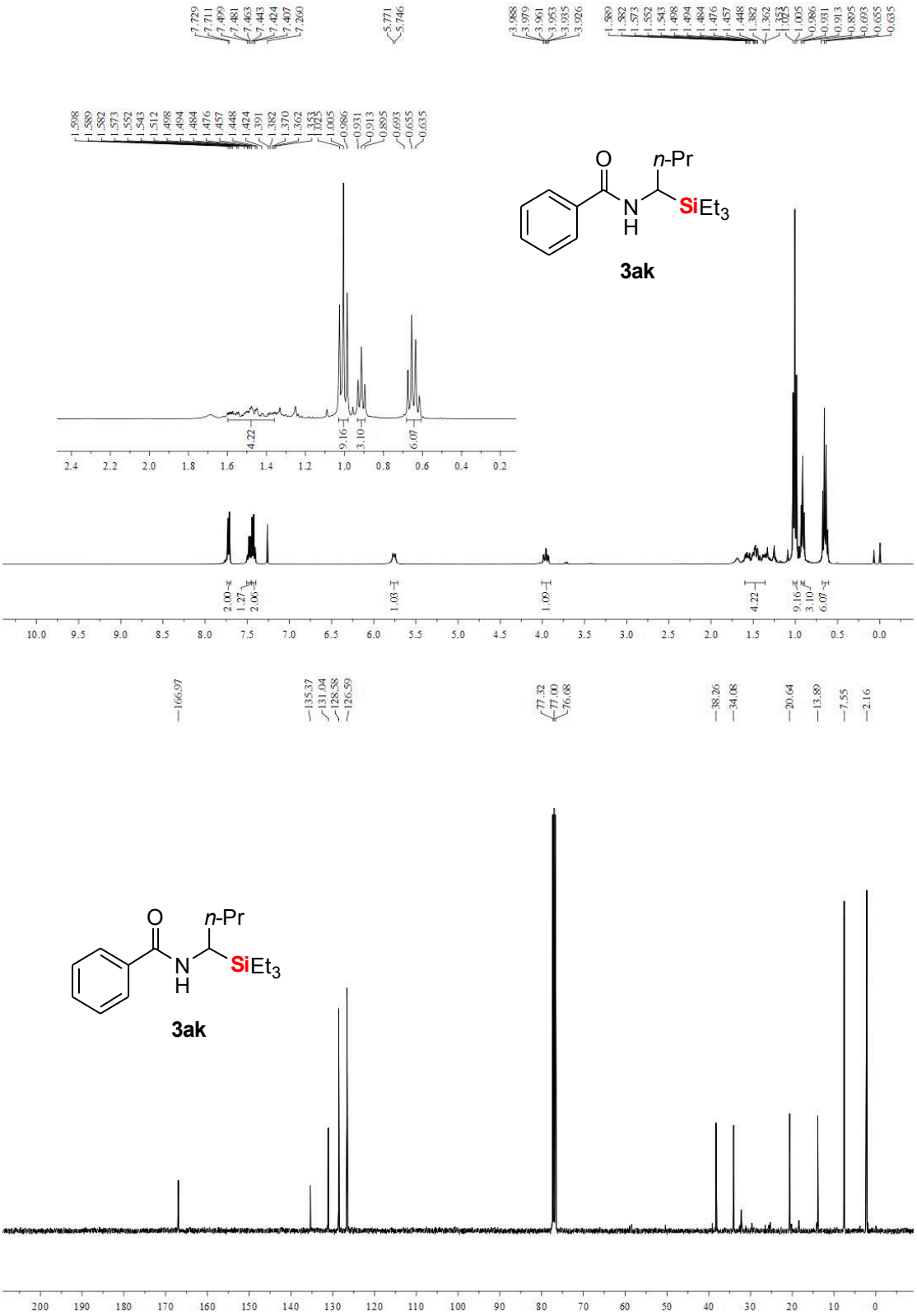
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ah



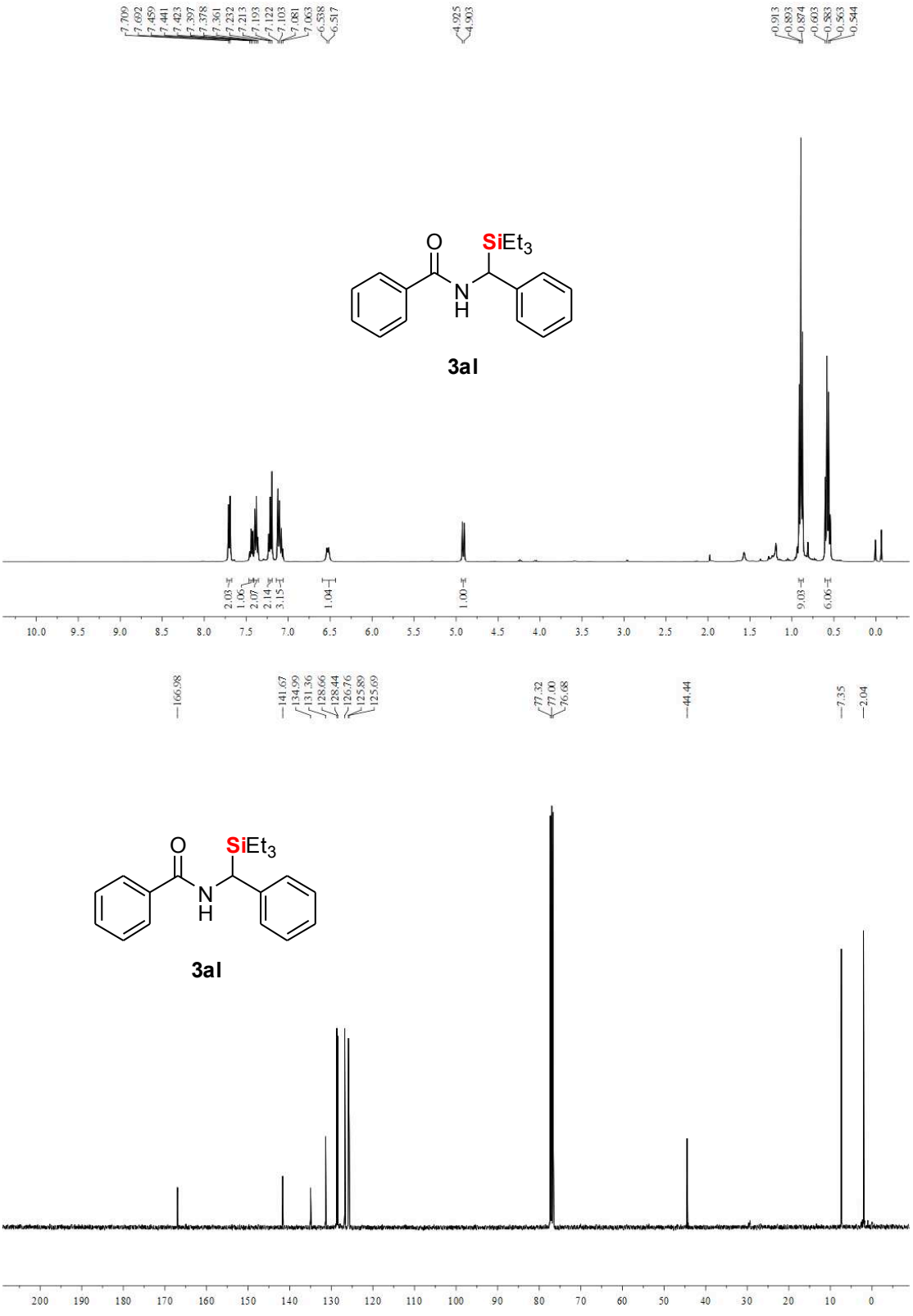
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ai



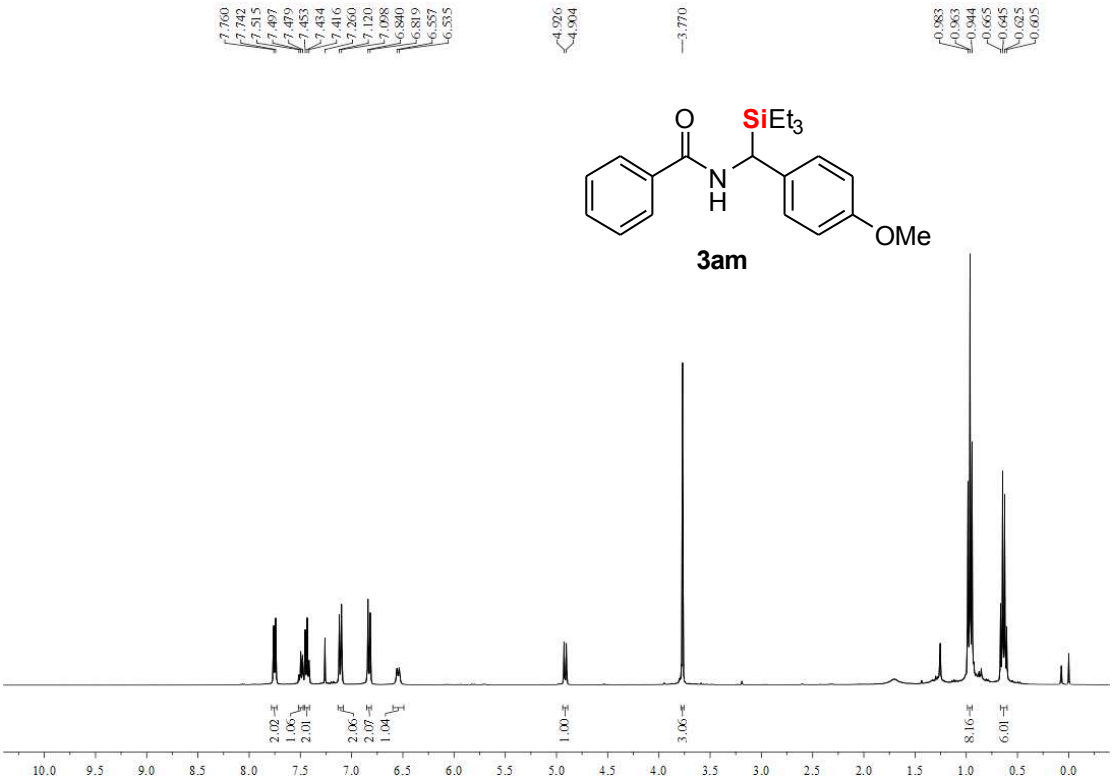
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3aj



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ak



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3al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H
OMe
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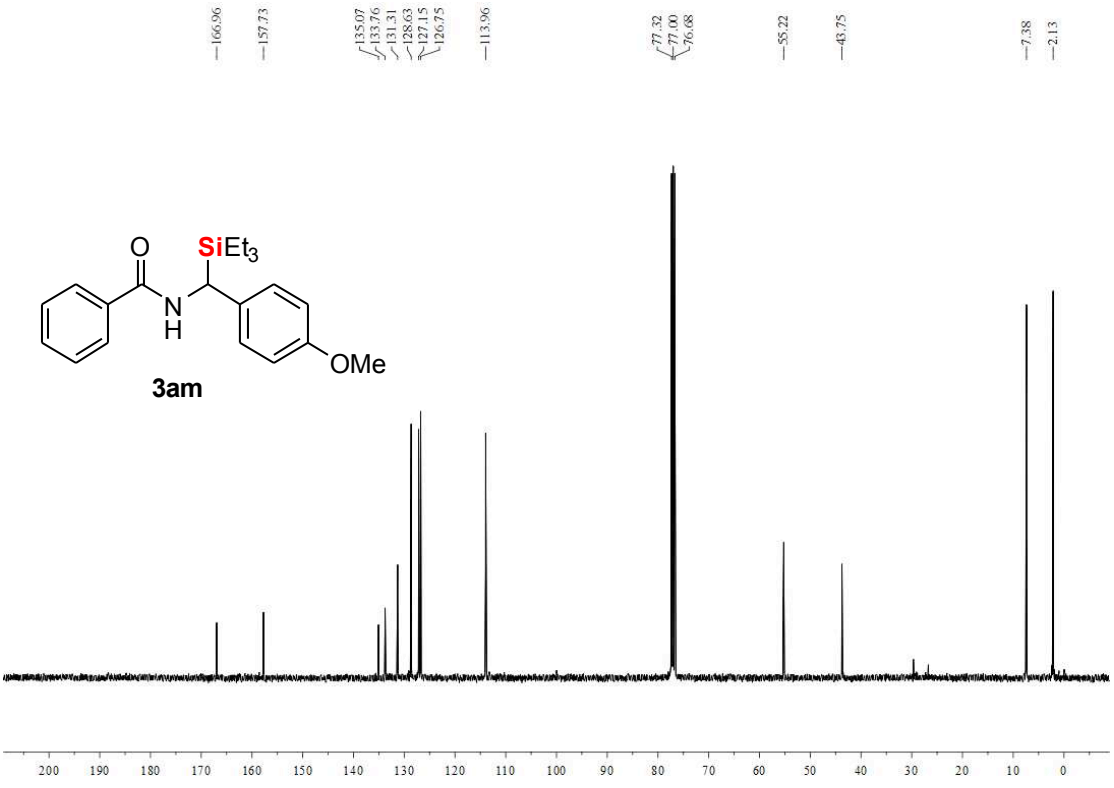
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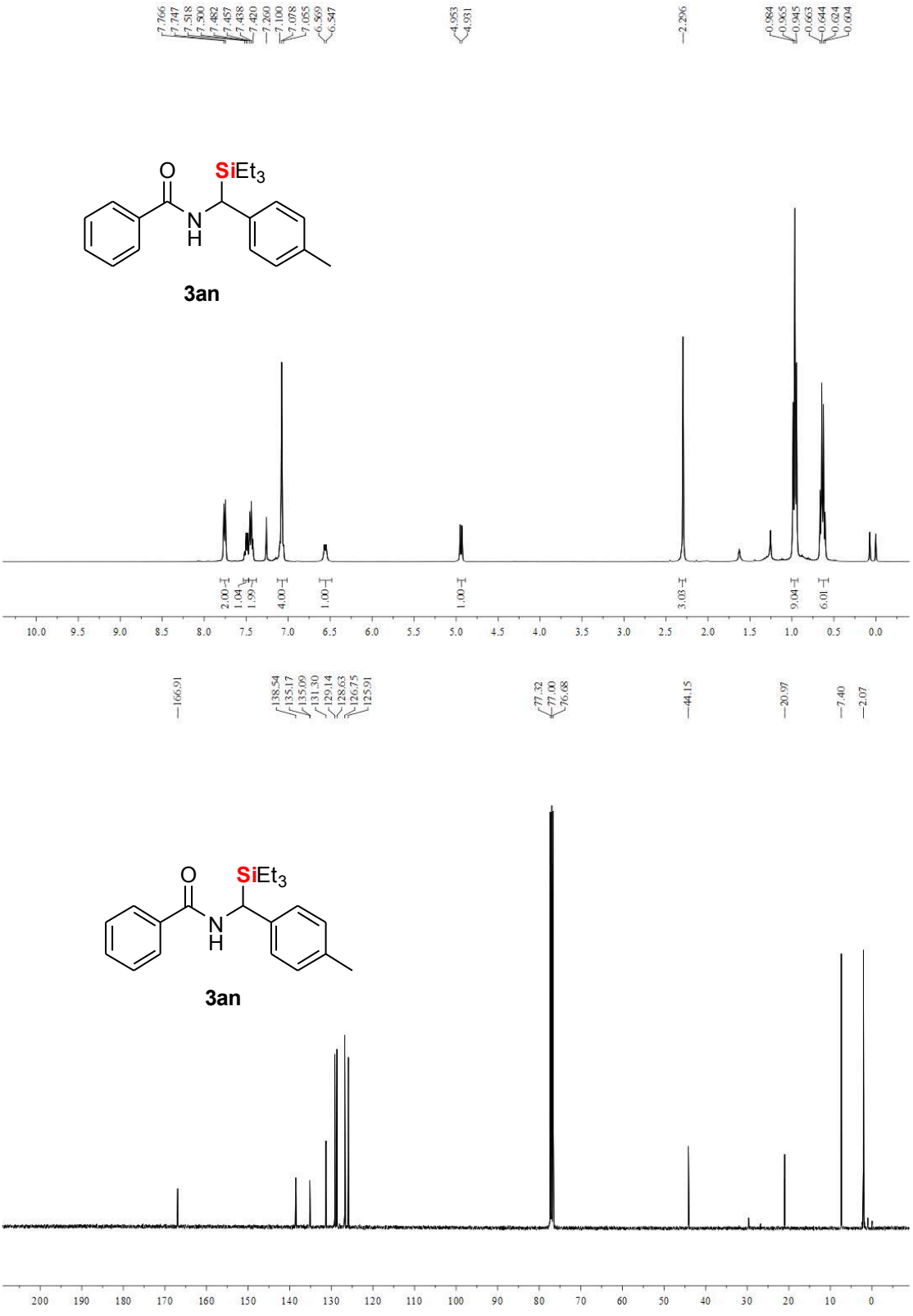
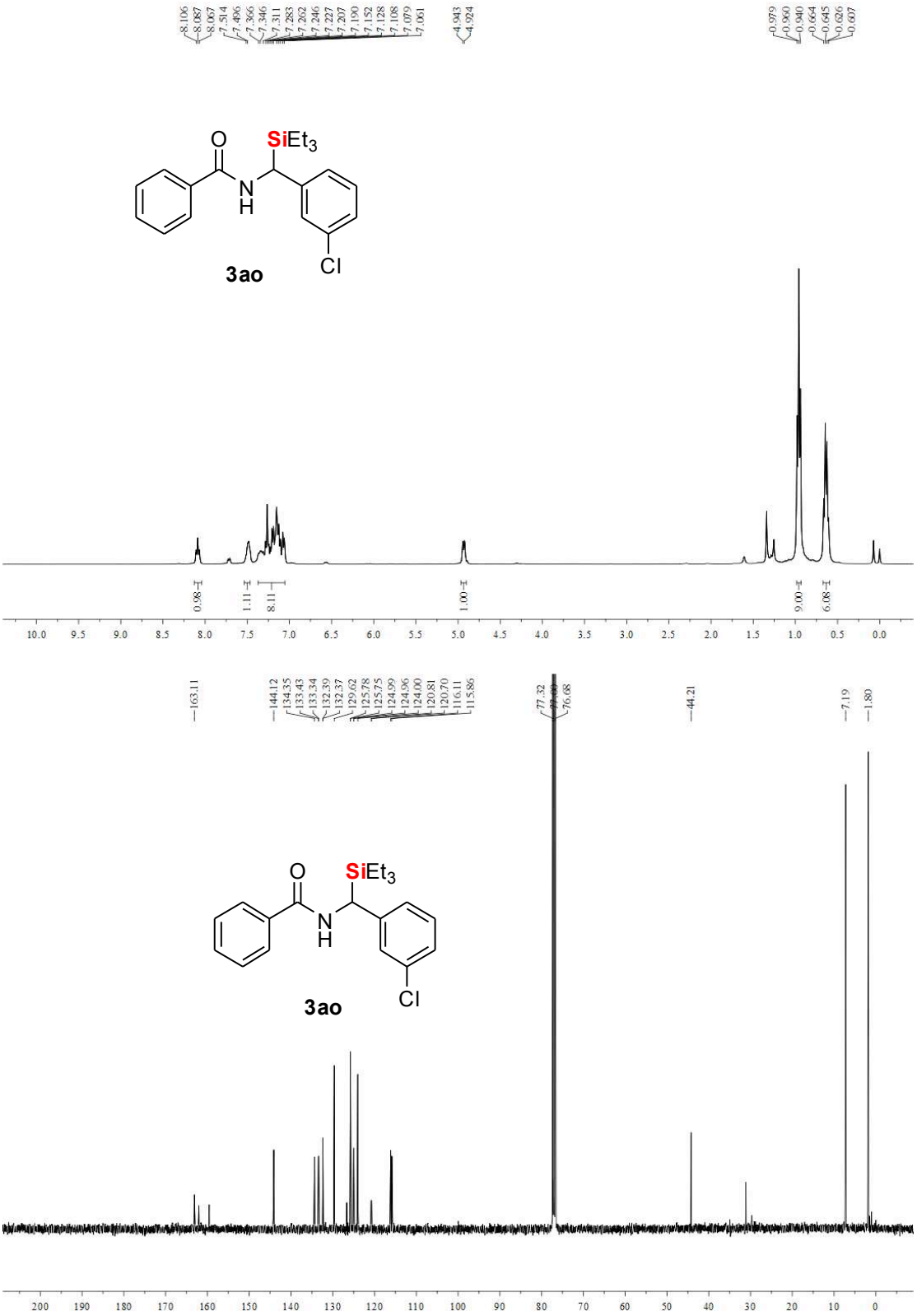
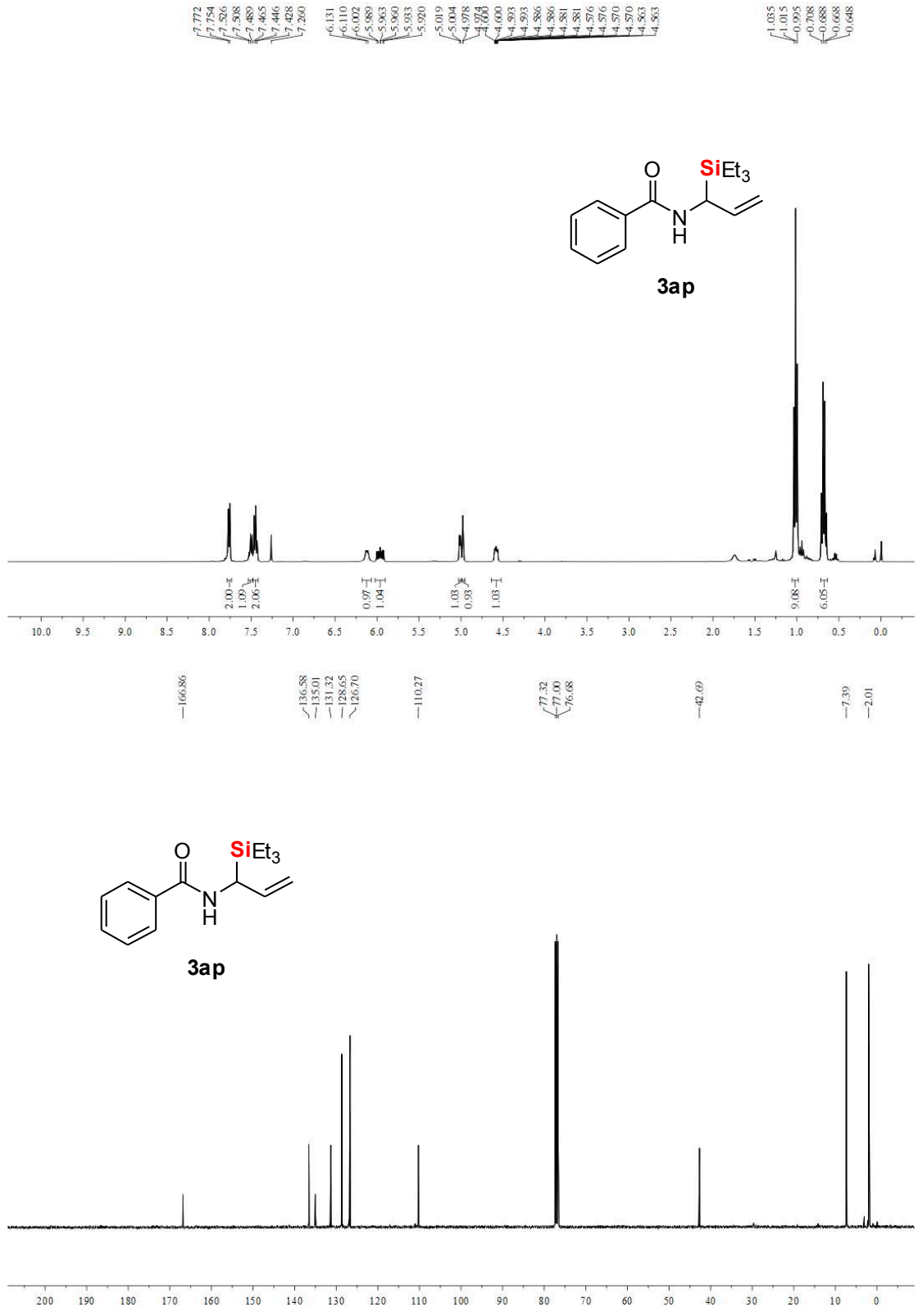


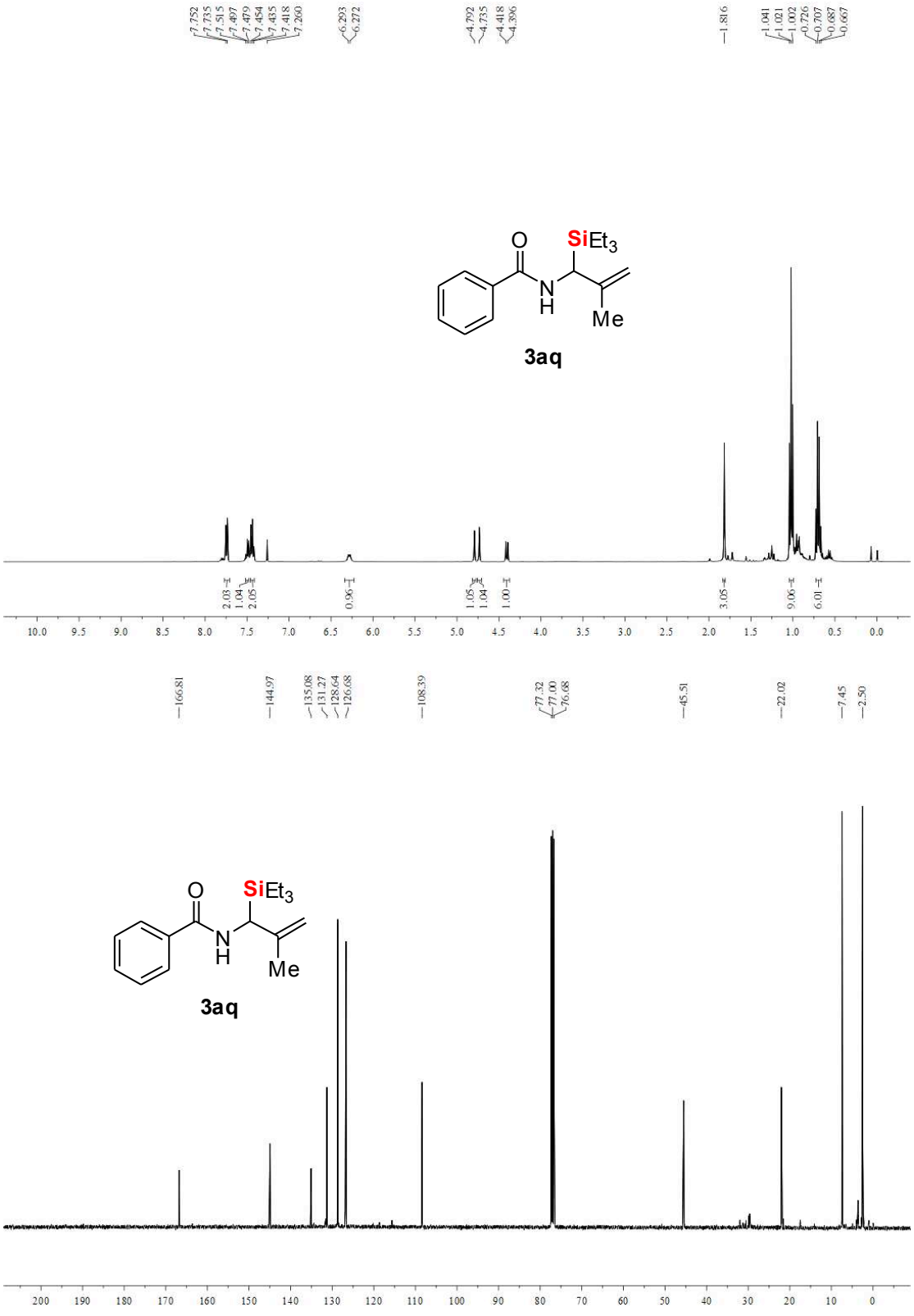
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3an



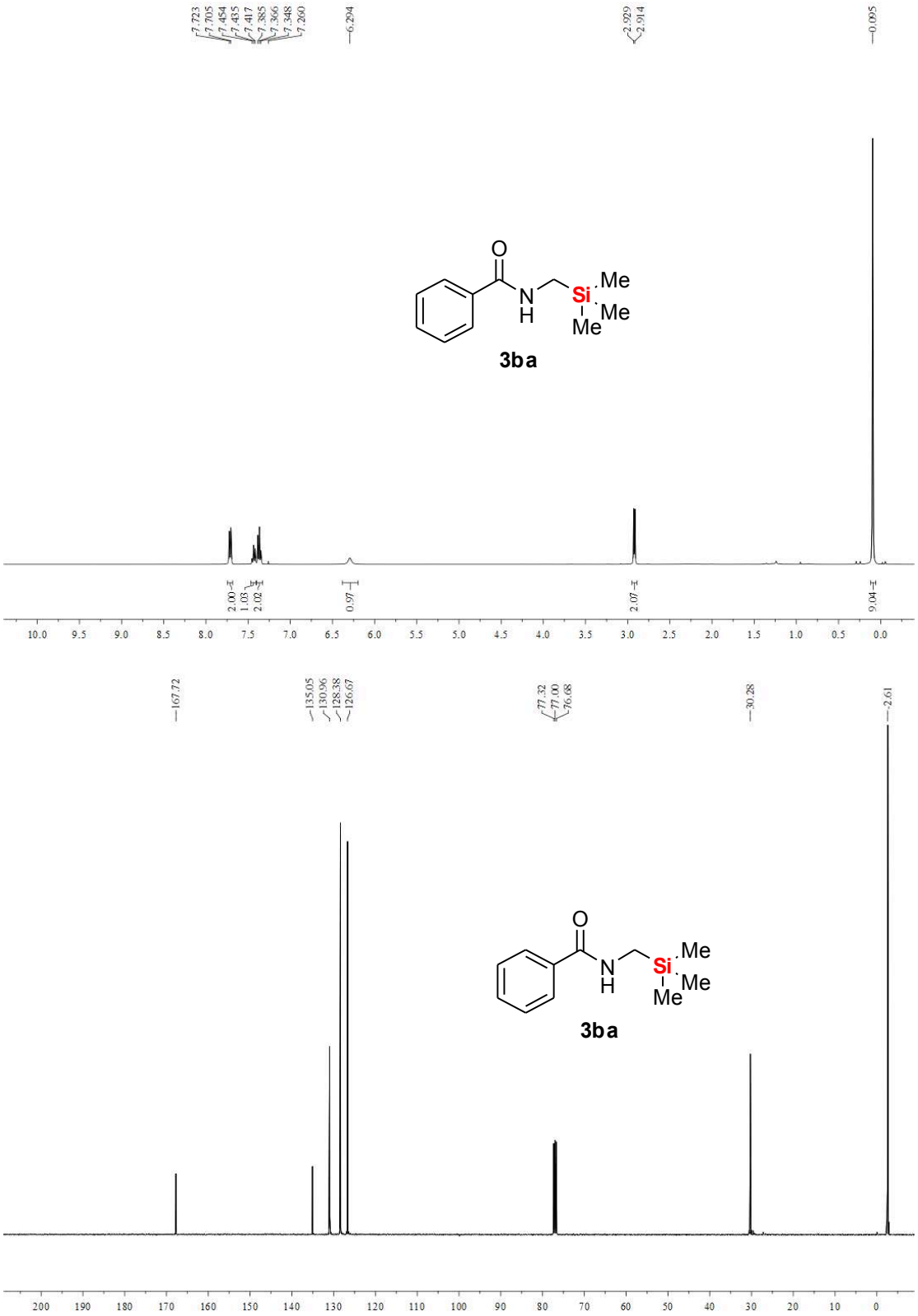
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ao



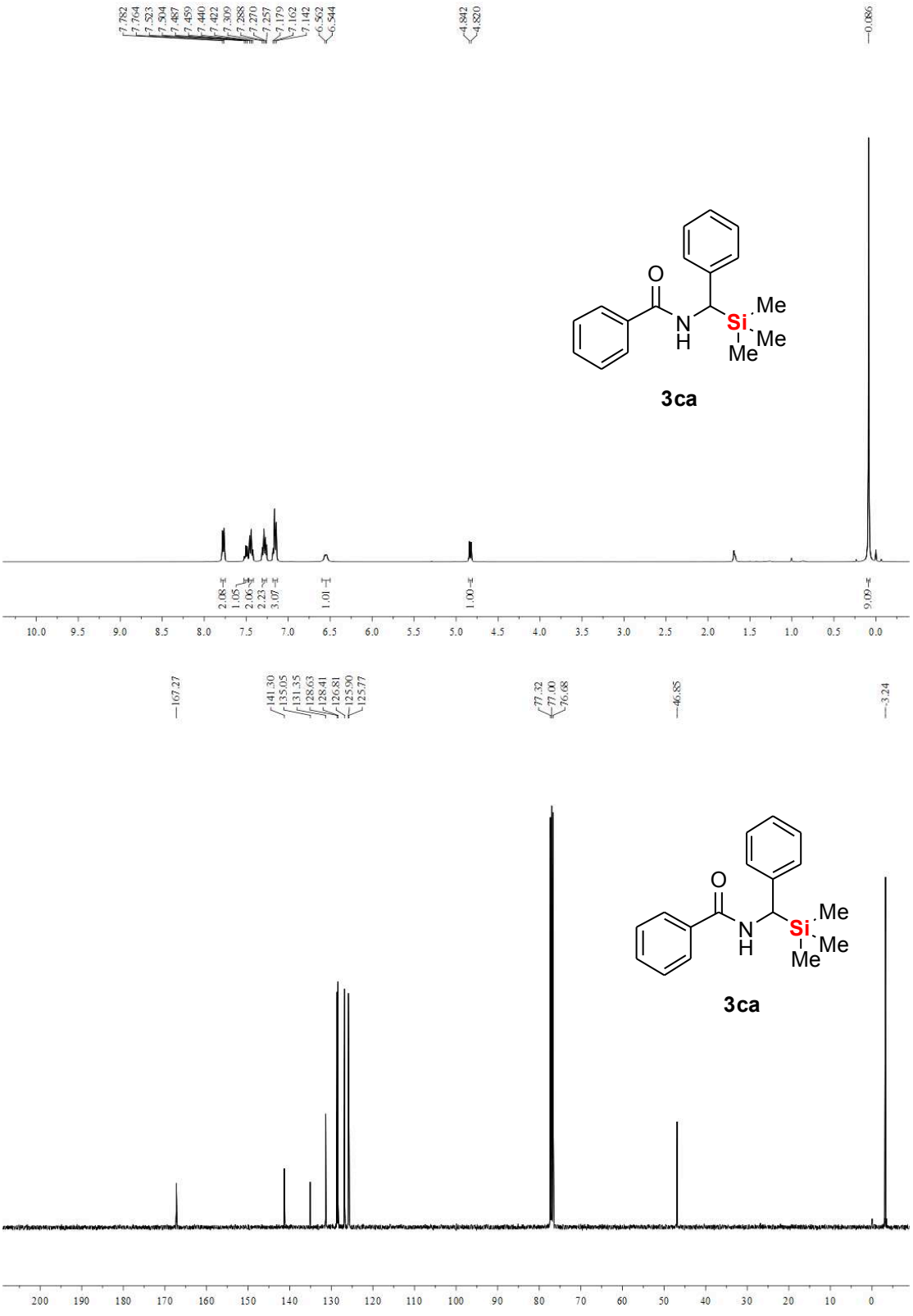
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ap



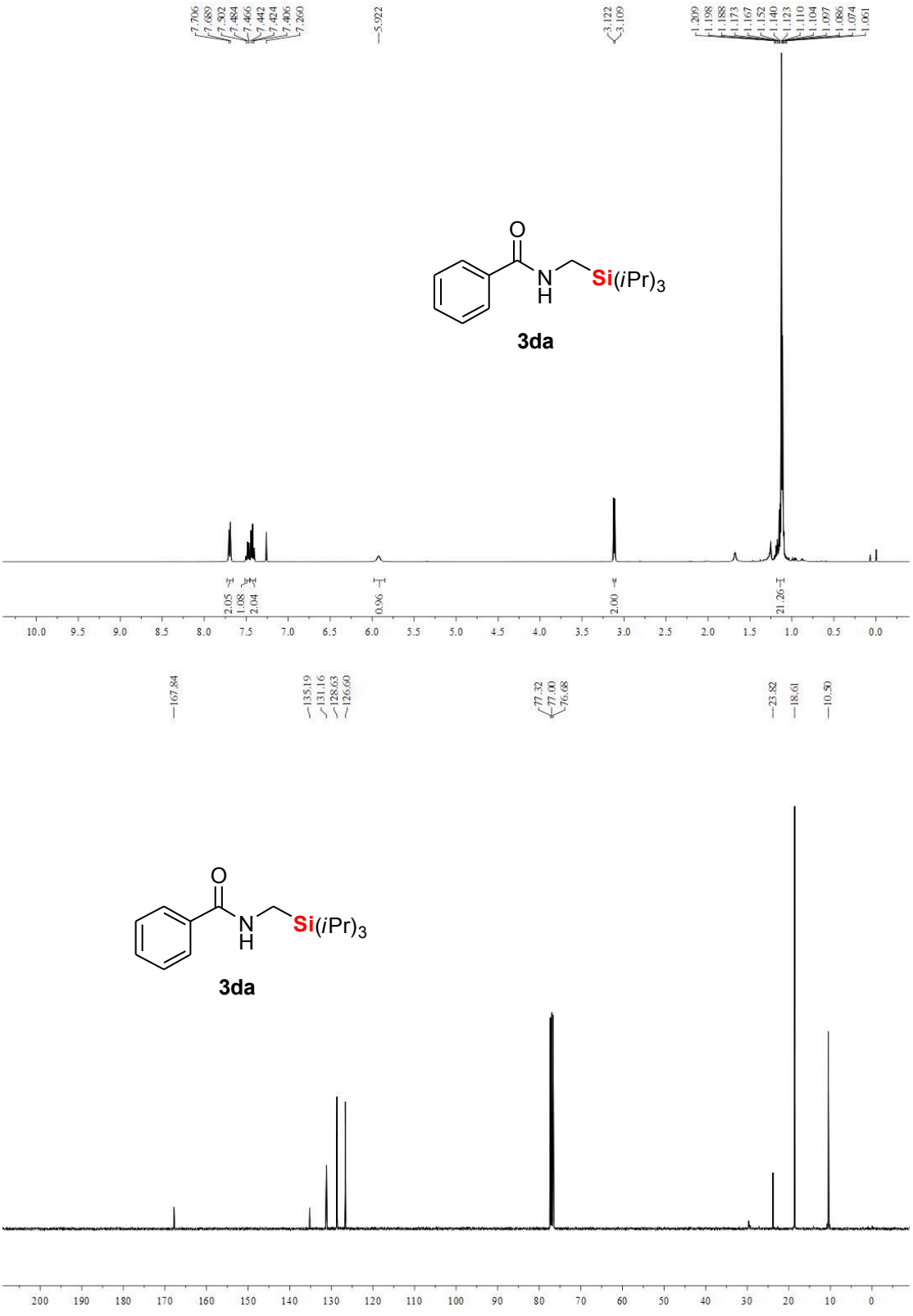
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3aq



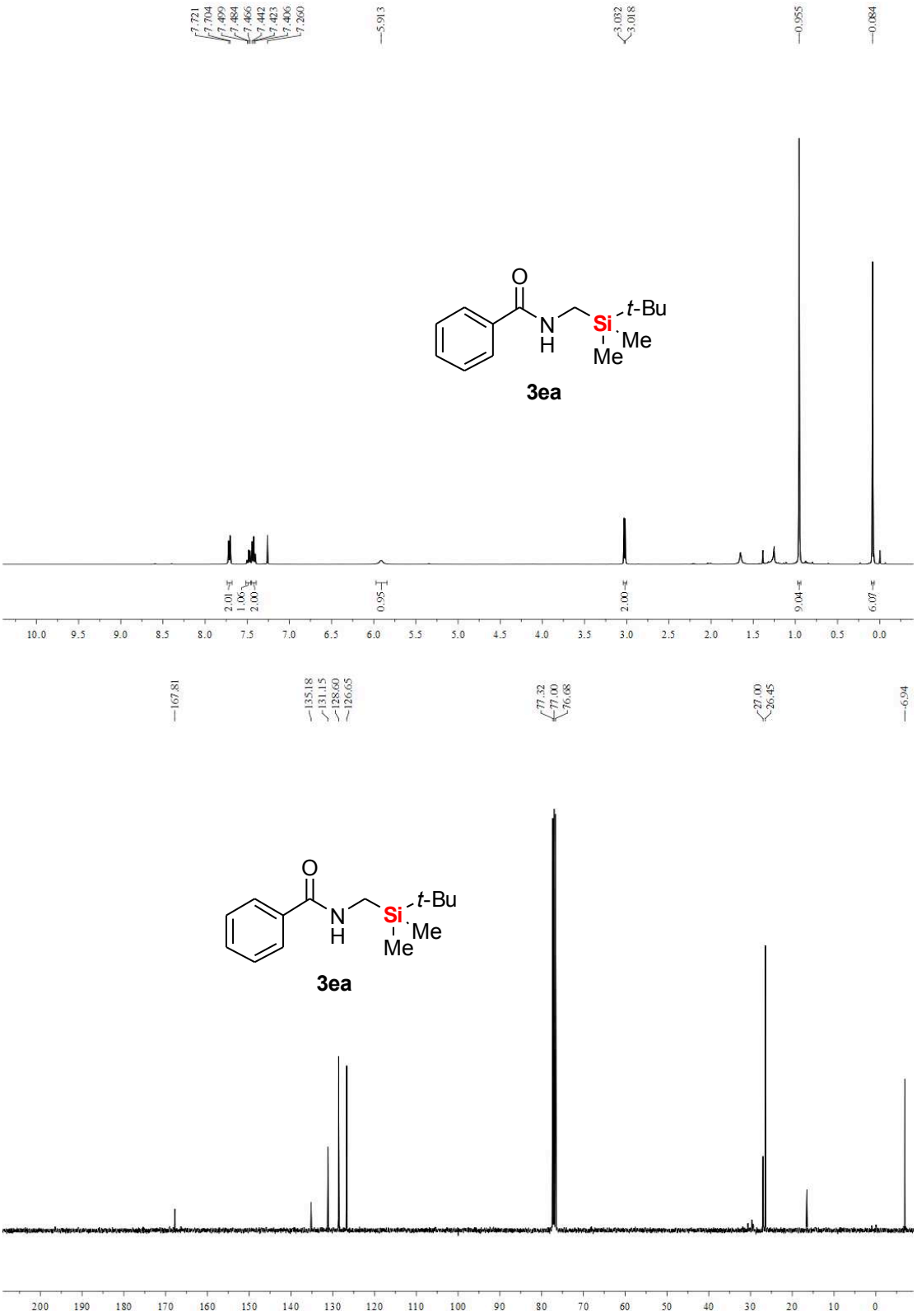
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ba



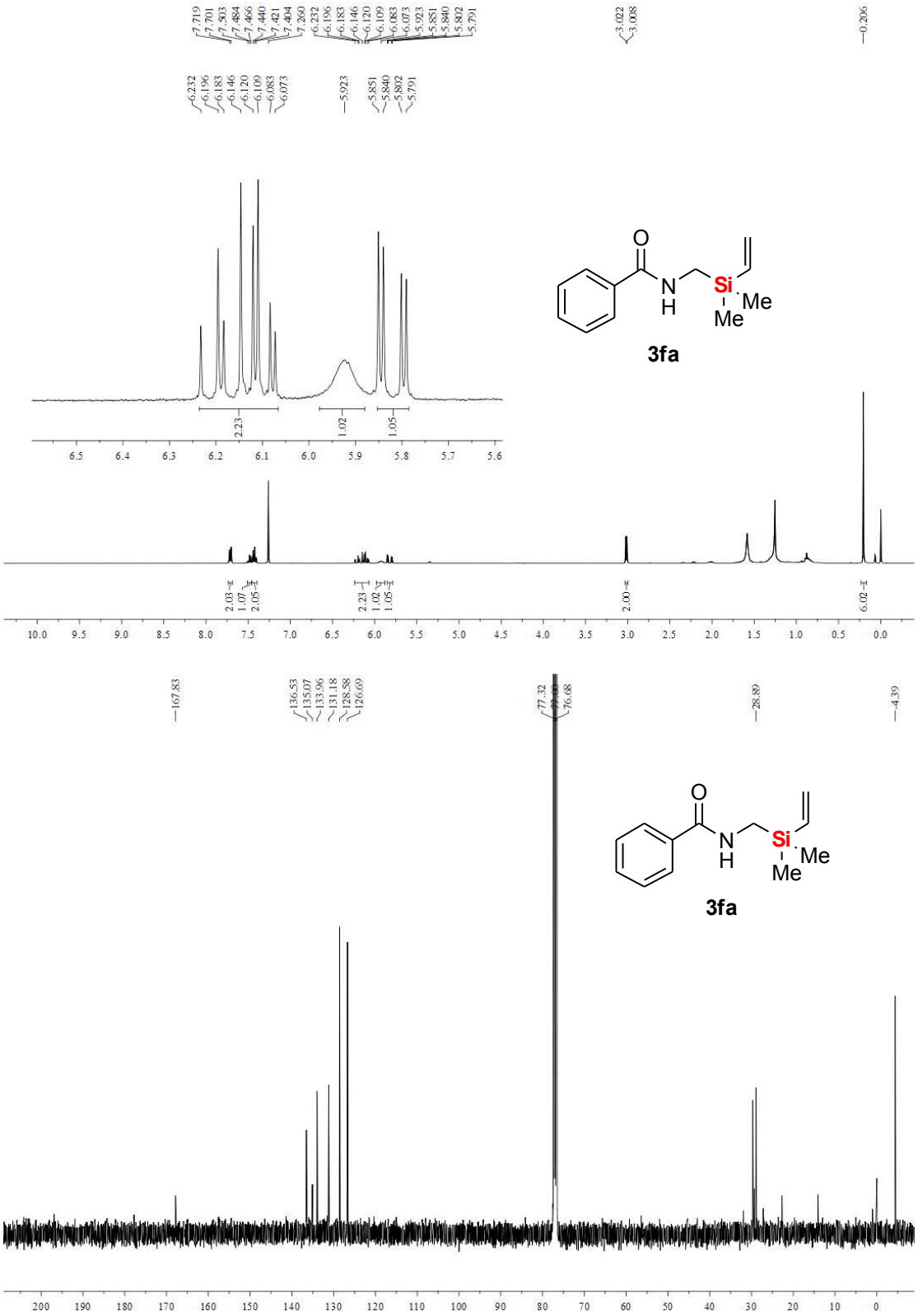
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ca



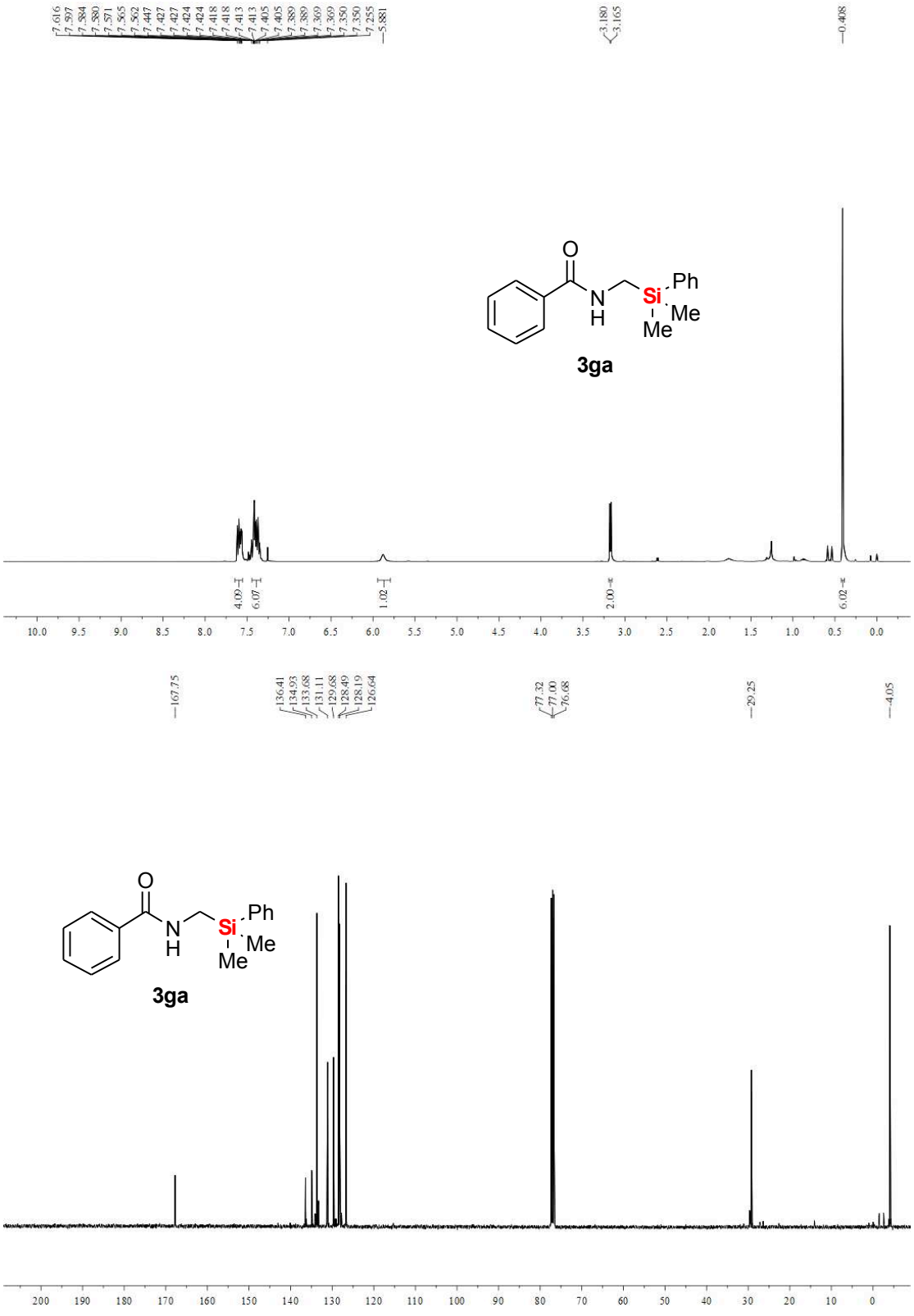
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3da



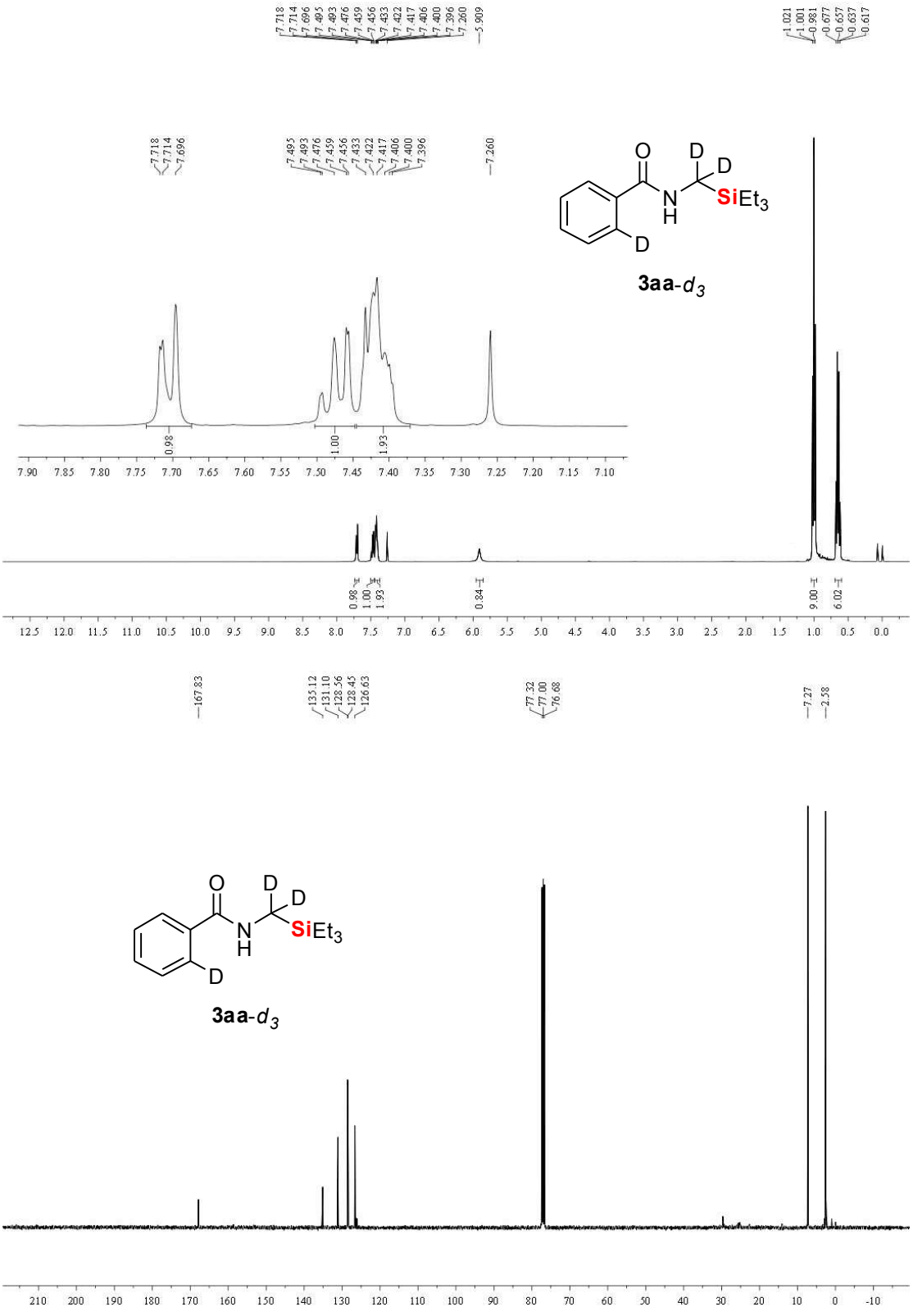
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ea



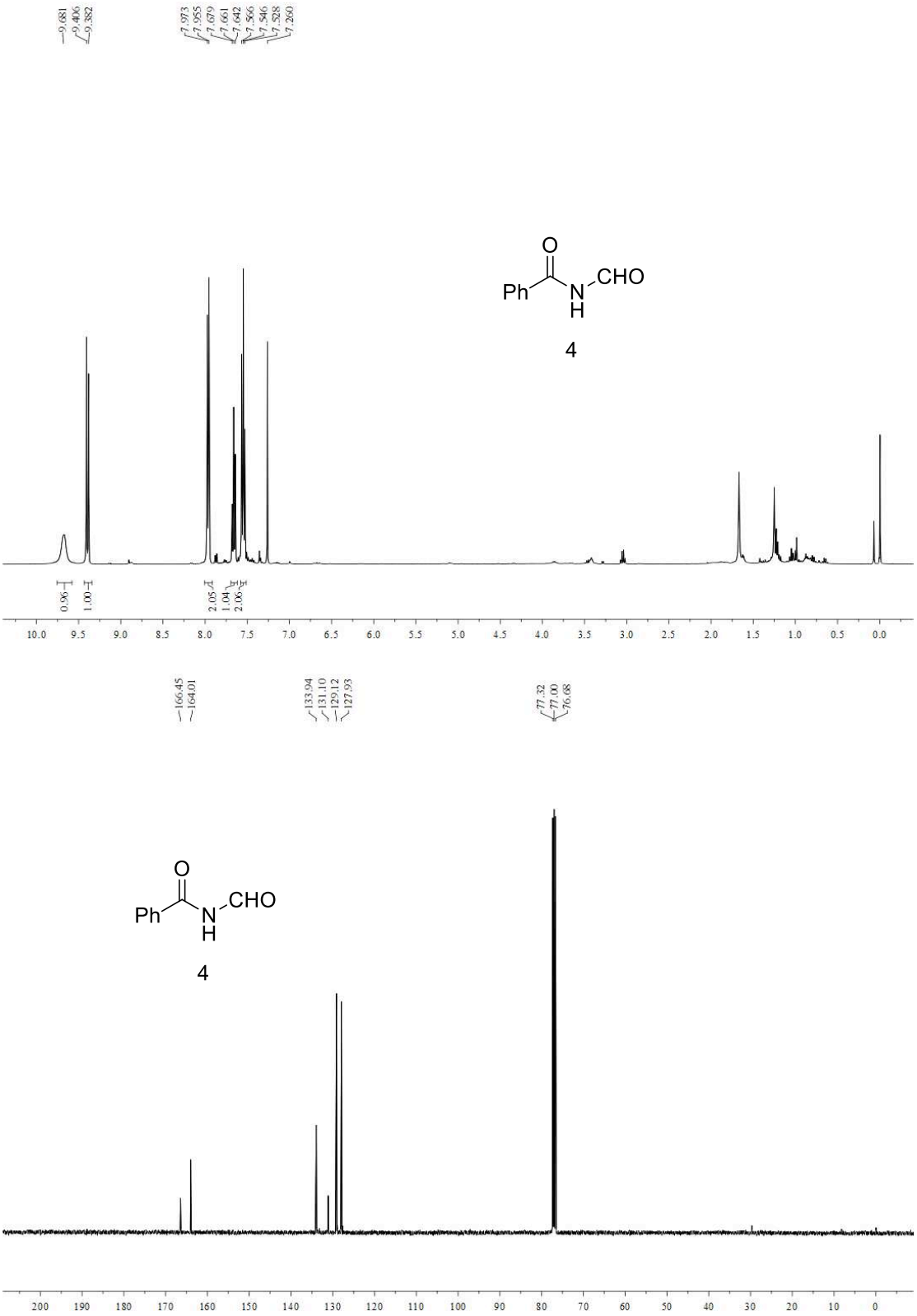
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3fa



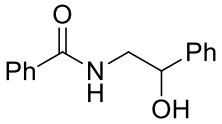
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ga



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3aa-d_3



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 4



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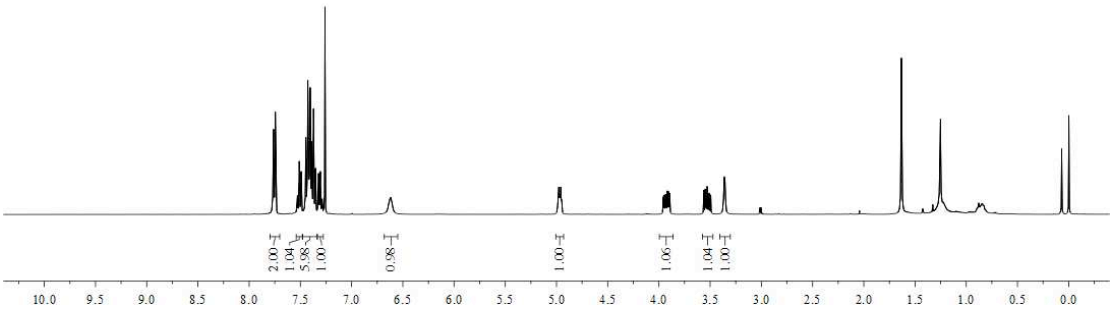

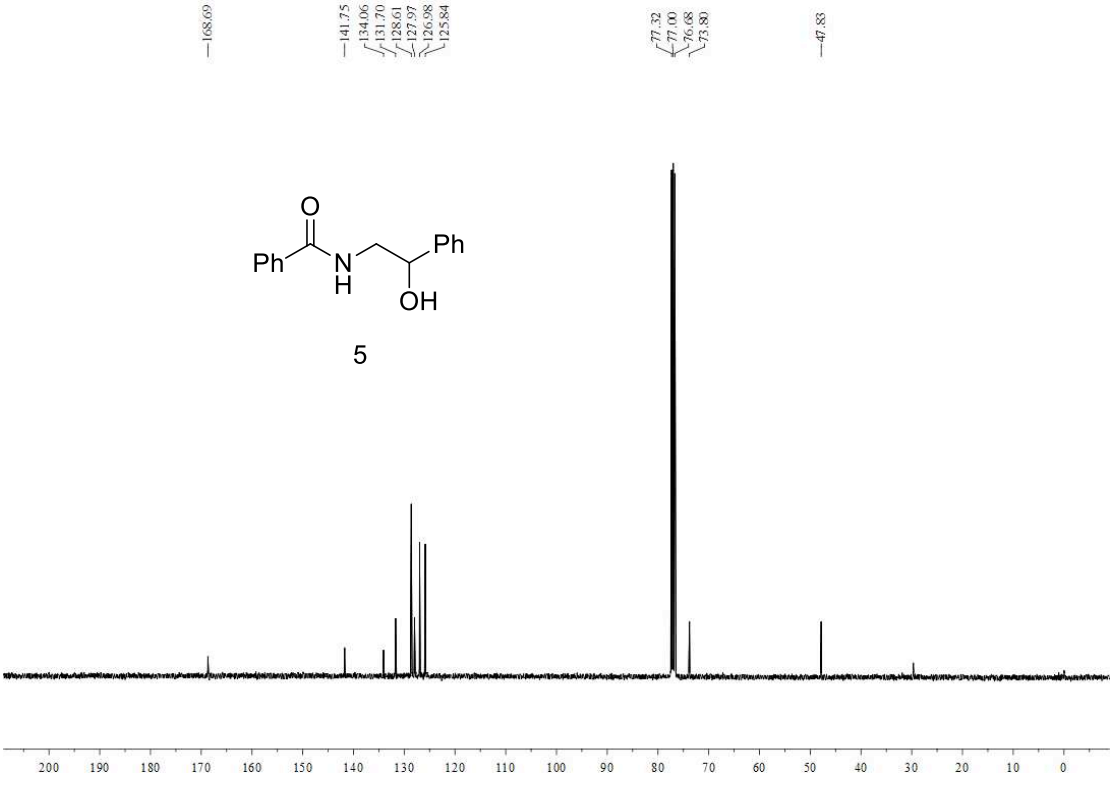

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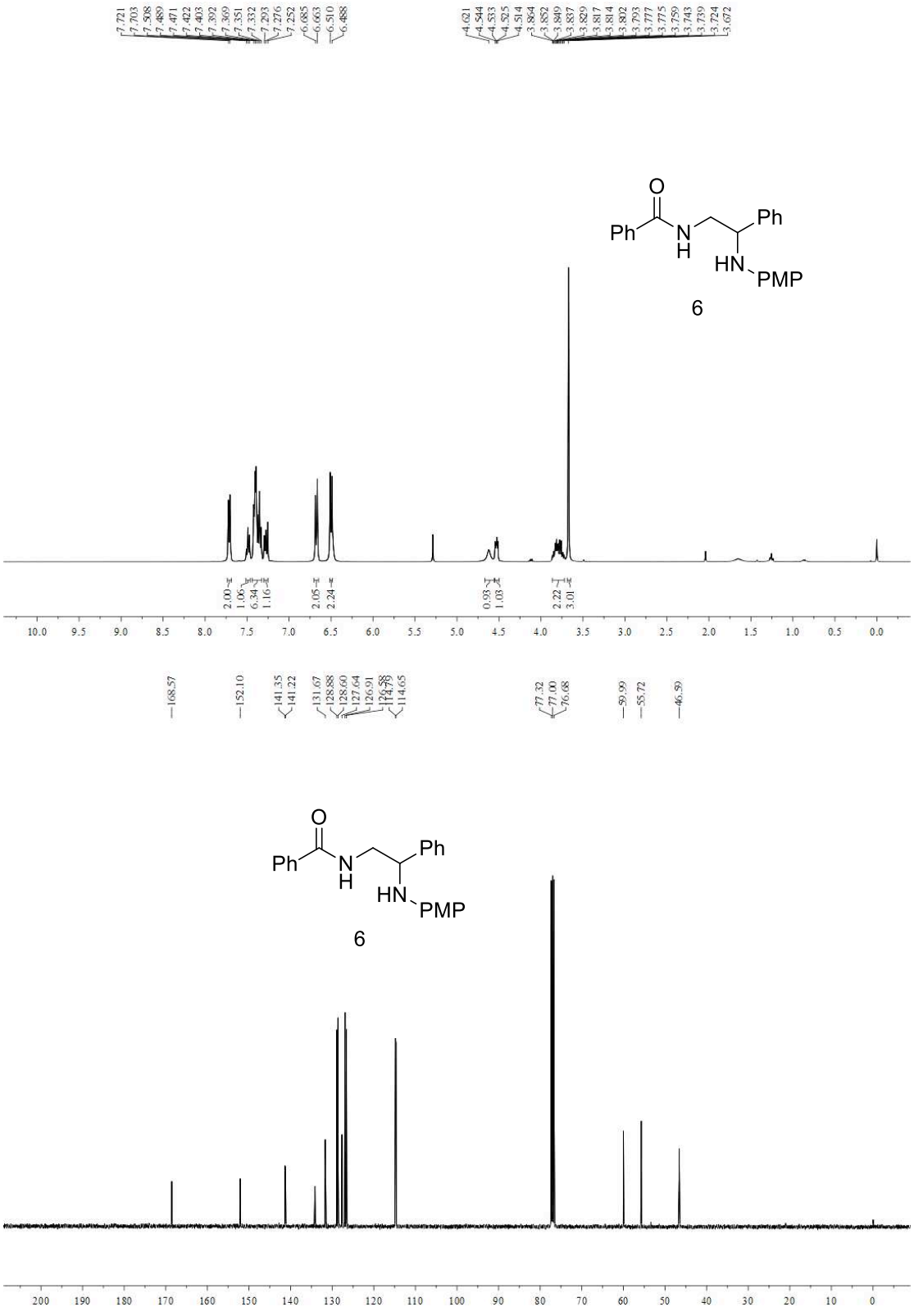
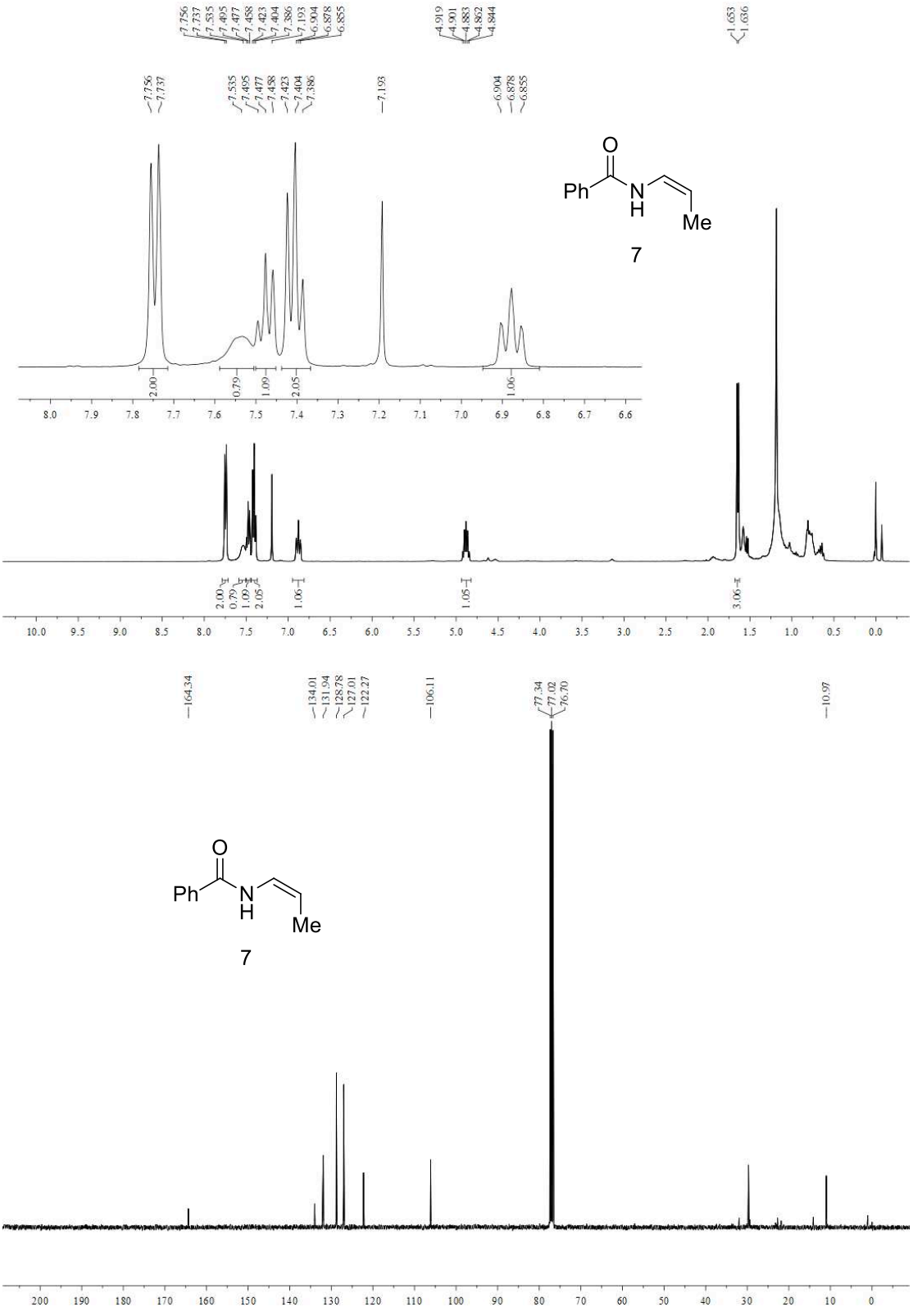
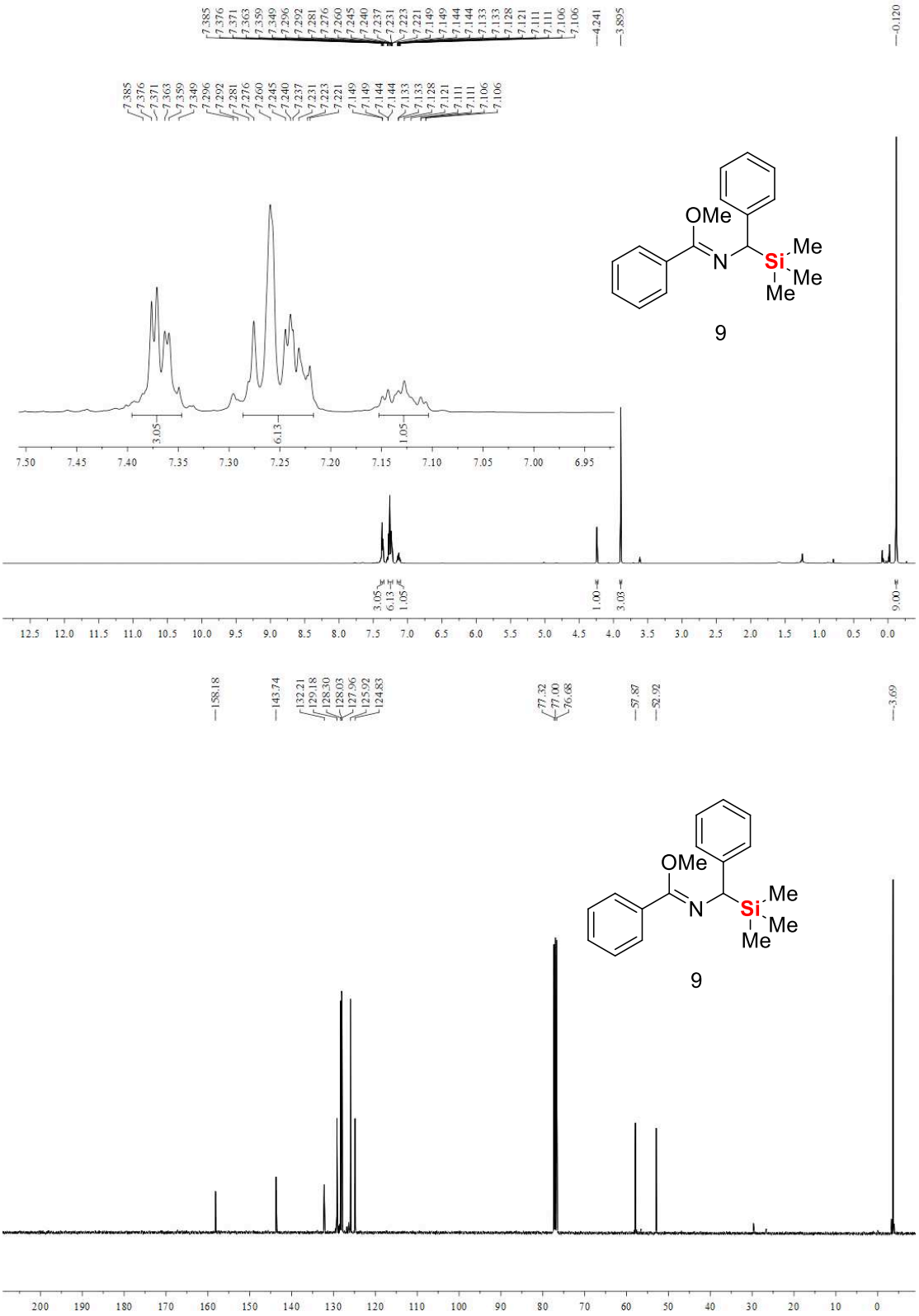
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 5



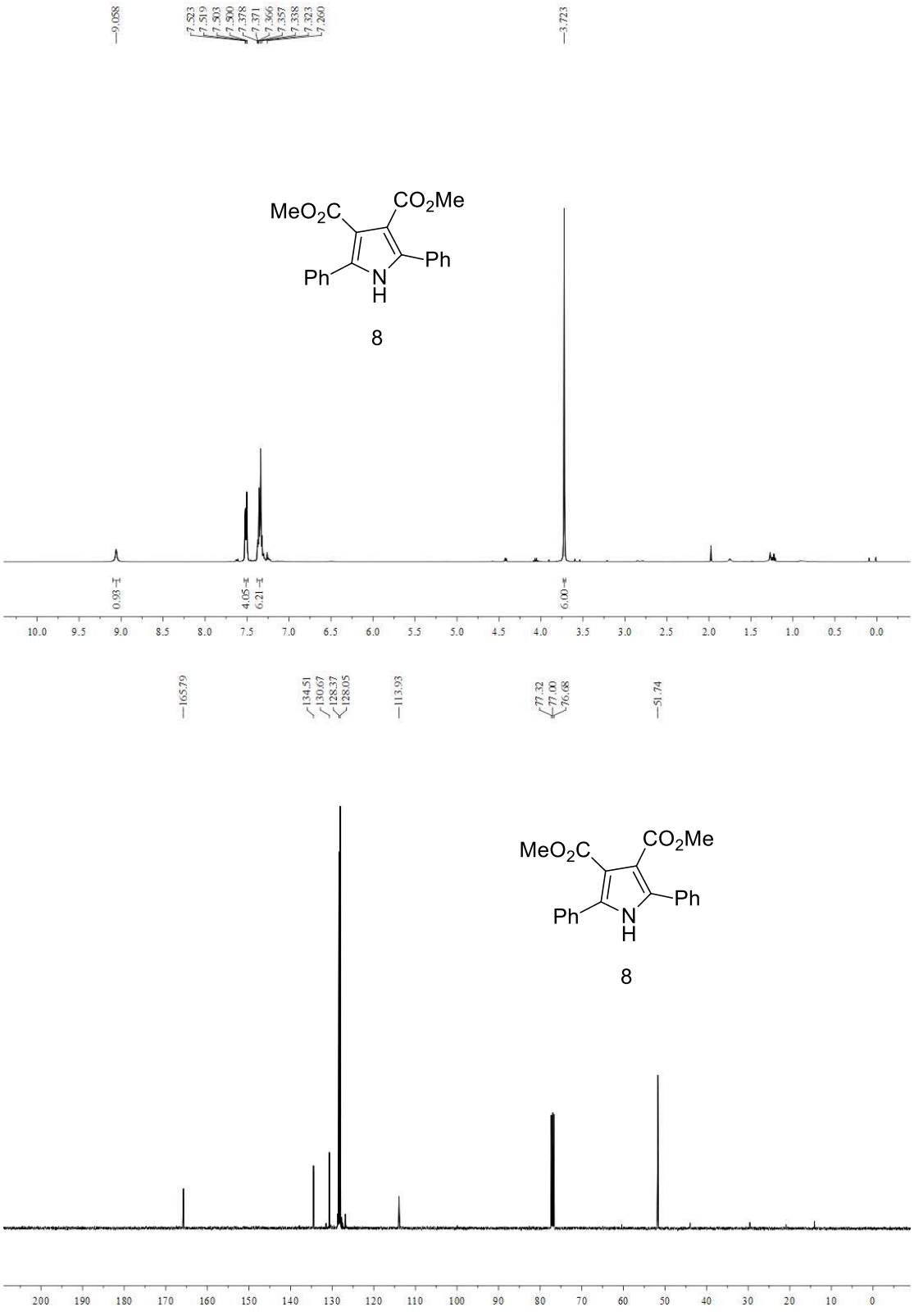
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 6



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 7



^{1}H and ^{13}C NMR spectra (in $CDCl_3$) for intermediate 9 in the synthesis of pyrrole 8



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 8