Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iron-catalyzed *para*-selective C–H silylation of benzamide derivatives with chlorosilanes

Pei Liu, Na Hao, Dong Yang, Lingyun Wan, Tianyi Wang, Tao Zhang, Rui Zhou, Xuefeng Cong, Jie Kong

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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, Adamas, 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.

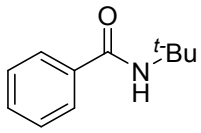
2. Procedure for the Preparation of Substituted benzamides

General procedure A: Benzoyl chlorides was slowly dropwised into the solution of *tert*-butylamine (1.5 equiv, aqueous), Et_3N (2 equiv) and DCM (2 M) at ice-water bath. Then the mixture was warmed to room temperature and stirred for 3 h. The crude product was then purified by flash chromatography on silica gel to give the corressponing benzamides (85–96% yields).

General procedure B: In a dried flask, substituted benzoic 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.

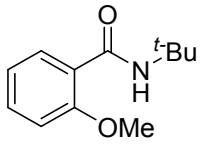
The prepared benzoyl chlorides was added to the solution of *tert*-butylamine (1.5 equiv, aqueous), Et_3N (2 equiv) and DCM (2 M) at ice-water bath. Then the mixture was warmed to room temperature and stirred for 3 h. The crude product was then purified by flash chromatography on silica gel to give the corressponing benzamides (60–96% yields).



***N*-(*tert*-butyl)benzamide (1a)**

The title compound was prepared according the **General procedure A**

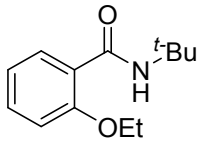
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 7.0 Hz, 2H), 7.48–7.44(m, 1H), 7.41–7.37 (m, 2H), 5.97 (brs, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.9, 135.9, 131.0, 128.4, 126.6, 51.5, 28.8. Spectroscopic data are in accordance with those described in the literature.[1]



***N*-(*tert*-butyl)-2-methoxybenzamide (1b)**

The title compound was prepared according the **General procedure B**

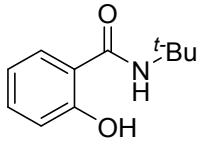
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (dd, J = 7.8, 1.8 Hz, 1H), 7.84 (brs, 1H), 7.42–7.33 (m, 1H), 7.08–7.00 (m, 1H), 6.93 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.1, 157.1, 132.3, 131.8, 122.6, 121.2, 111.2, 55.8, 50.9, 28.8. Spectroscopic data are in accordance with those described in the literature.[2]



***N*-(*tert*-butyl)-2-ethoxybenzamide (1c)**

The title compound was prepared according the **General procedure A**

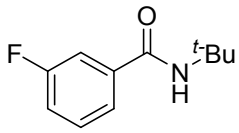
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (dd, J = 7.8, 1.8 Hz, 1H), 8.12 (brs, 1H), 7.42–7.35 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 4.16 (q, J = 7.0 Hz, 2H), 1.52 (t, J = 7.0 Hz, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.1, 156.7, 132.3, 131.9, 122.5, 121.2, 112.1, 64.6, 51.1, 28.9, 14.8. HRMS (ESI$^+$): calcd for $C_{13}H_{19}NO_2Na$ $[M+Na]^+$ 244.13135, found 244.13018.



***N*-(*tert*-butyl)-2-hydroxybenzamide (1d)**

The title compound was prepared according the **General procedure B**

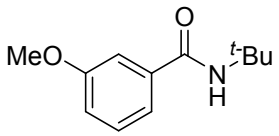
^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.50 (brs, 1H), 7.38–7.33 (m, 1H), 7.28 (dd, J = 8.0, 1.4 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.84–6.78 (m, 1H), 6.11 (brs, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.7, 161.6, 133.8, 125.2, 118.6, 118.4, 115.1, 52.1, 28.8. Spectroscopic data are in accordance with those described in the literature.[3]



***N*-(*tert*-butyl)-3-fluorobenzamide (1e)**

The title compound was prepared according the **General procedure A**

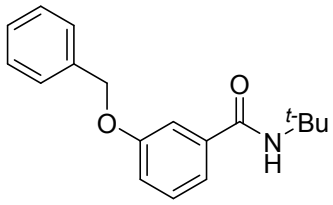
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47–7.40 (m, 2H), 7.39–7.33 (m, 1H), 7.17–7.12 (m, 1H), 5.96 (brs, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.5 (d, J = 2.0 Hz), 162.7 (d, J = 246.0 Hz), 138.2 (d, J = 7.0 Hz), 130.0 (d, J = 8.0 Hz), 122.1 (d, J = 3.0 Hz), 118.0 (d, J = 21.0 Hz), 114.1 (d, J = 23.0 Hz), 51.8, 28.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -112.09. Spectroscopic data are in accordance with those described in the literature.[1]



***N*-(*tert*-butyl)-3-methoxybenzamide (1f)**

The title compound was prepared according the **General procedure A**

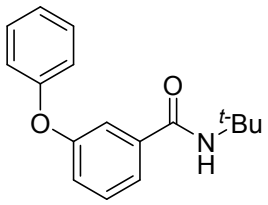
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34–7.27 (m, 2H), 7.21 (d, J = 7.7 Hz, 1H), 7.00 (dd, J = 8.1, 2.0 Hz, 1H), 5.95 (brs, 1H), 3.84 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7, 159.8, 137.4, 129.4, 118.3, 117.3, 112.1, 55.4, 51.6, 28.8. Spectroscopic data are in accordance with those described in the literature.[2]



3-(benzyloxy)-N-(tert-butyl)benzamide (1g)

The title compound was prepared according the **General procedure B**

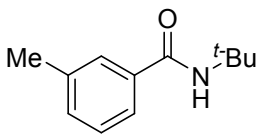
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.21 (m, 8H), 7.05 (dd, J = 7.9, 1.4 Hz, 1H), 5.95 (brs, 1H), 5.07 (s, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 158.8, 137.4, 136.5, 129.4, 128.6, 128.0, 127.5, 118.8, 117.9, 113.1, 70.1, 51.5, 28.8. HRMS (ESI$^+$): calcd for $C_{18}H_{21}NO_2Na$ $[M+Na]^+$ 306.14700, found 306.14577.



***N*-(*tert*-butyl)-3-phenoxybenzamide (1h)**

The title compound was prepared according the **General procedure B**

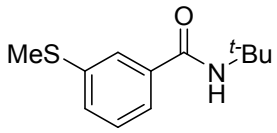
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.32 (m, 5H), 7.15–7.08 (m, 2H), 7.03–6.98 (m, 2H), 5.91 (brs, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.2, 157.6, 156.7, 137.8, 129.9, 129.8, 123.7, 121.3, 121.2, 119.1, 117.2, 51.7, 28.8. HRMS (ESI$^+$): calcd for $C_{17}H_{19}NO_2Na$ $[M+Na]^+$ 292.13135, found 292.13005.



***N*-(*tert*-butyl)-3-methylbenzamide (1i)**

The title compound was prepared according the **General procedure A**

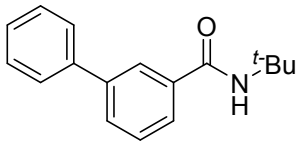
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 7.46–7.43 (m, 1H), 7.25–7.20 (m, 2H), 5.92 (brs, 1H), 2.34 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.1, 138.2, 135.8, 131.7, 128.3, 127.4, 123.6, 51.5, 28.8, 21.3. Spectroscopic data are in accordance with those described in the literature.[2]



***N*-(*tert*-butyl)-3-(methylthio)benzamide (1j)**

The title compound was prepared according the **General procedure B**

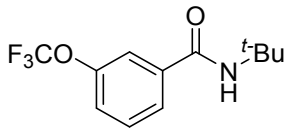
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, J = 1.5 Hz, 1H), 7.41–7.36 (m, 1H), 7.35–7.26 (m, 2H), 5.96 (brs, 1H), 2.49 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4, 139.4, 136.5, 128.8, 128.7, 124.7, 122.8, 51.6, 28.8, 15.6. HRMS (ESI$^+$): calcd for $C_{12}H_{17}NOSNa$ $[M+Na]^+$ 246.09285, found 246.09173.



***N*-(*tert*-butyl)-[1,1'-biphenyl]-3-carboxamide (1k)**

The title compound was prepared according the **General procedure B**

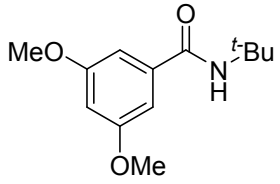
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (t, J = 1.7 Hz, 1H), 7.71–7.65 (m, 2H), 7.63–7.59 (m, 2H), 7.50–7.43 (m, 3H), 7.40–7.35 (m, 1H), 6.02 (brs, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.9, 141.5, 140.3, 136.5, 129.7, 128.82, 128.79, 127.6, 127.1, 125.6, 125.3, 51.6, 28.8. Spectroscopic data are in accordance with those described in the literature.[4]



***N*-(*tert*-butyl)-3-(trifluoromethoxy)benzamide (1l)**

The title compound was prepared according the **General procedure B**

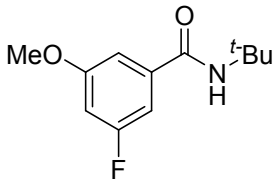
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62–7.56 (m, 2H), 7.42 (dd, J = 9.8, 5.7 Hz, 1H), 7.31 (s, 1H), 5.98 (brs, 1H), 1.46 (d, J = 2.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.3, 149.3, 138.0, 129.9, 124.8, 123.4, 119.7, 51.7, 28.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -57.8. HRMS (ESI$^+$): calcd for $C_{12}H_{14}NO_2F_3Na$ $[M+Na]^+$ 284.08743, found 284.08602.



***N*-(*tert*-butyl)-3,5-dimethoxybenzamide (1m)**

The title compound was prepared according the **General procedure B**

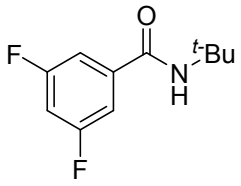
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83 (d, J = 2.3 Hz, 2H), 6.53 (t, J = 2.3 Hz, 1H), 5.93 (brs, 1H), 3.80 (s, 6H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 160.7, 138.1, 104.6, 103.0, 55.5, 51.6, 28.8. Spectroscopic data are in accordance with those described in the literature.[5]



The title compound was prepared according the **General procedure B**

***N*-(*tert*-butyl)-3-fluoro-5-methoxybenzamide (1n)**

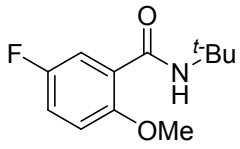
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.06 (s, 1H), 6.93 (d, J = 8.8 Hz, 1H), 6.72–6.65 (m, 1H), 5.91 (brs, 1H), 3.83–3.79 (m, 3H), 1.45 (d, J = 0.7 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.5 (d, J=3.0 Hz), 163.3 (d, J=245.0 Hz), 161.0 (d, J=11.0 Hz), 138.6 (d, J=8.0 Hz), 108.3 (d, J=2.0 Hz), 150.9 (d, J=23.0 Hz), 104.4 (d, J=25.0 Hz), 55.7, 51.8, 28.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -110.8. HRMS (ESI$^+$): calcd for $C_{12}H_{16}NO_2FNa$ $[M+Na]^+$ 248.10628, found 248.10499.



***N*-(*tert*-butyl)-3,5-difluorobenzamide (1o)**

The title compound was prepared according the **General procedure A**

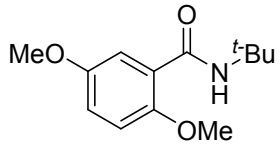
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24–7.15 (m, 2H), 6.94–6.83 (m, 1H), 5.96 (d, J = 56.0 Hz, 1H), 1.45 (d, J = 7.9 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.4, 162.9 (d, J=249.0 Hz), 139.3 (t, J=8.0 Hz), 110.0 (q, J=12.0 Hz), 106.3 (t, J=25.0 Hz), 52.0, 28.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -108.3. Spectroscopic data are in accordance with those described in the literature.[6]



***N*-(*tert*-butyl)-5-fluoro-2-methoxybenzamide (1p)**

The title compound was prepared according the **General procedure B**

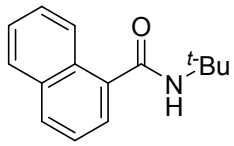
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (dd, J = 9.7, 3.3 Hz, 2H), 7.13–7.07 (m, 1H), 6.90 (dd, J = 9.0, 4.1 Hz, 1H), 3.93 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 158.4, 156.1, 153.3 (d, J=2.0 Hz), 124.4 (d, J=7.0 Hz), 118.4 (t, J=25.0 Hz), 118.1, 112.8, 56.5, 51.1, 28.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -122.2. HRMS (ESI$^+$): calcd for $C_{12}H_{16}NO_2FNa$ $[M+Na]^+$ 248.10628, found 248.10500.



***N*-(*tert*-butyl)-2,5-dimethoxybenzamide (1q)**

The title compound was prepared according the **General procedure B**

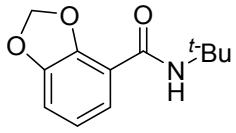
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (brs, 1H), 7.75 (d, J = 3.2 Hz, 1H), 6.96 (dd, J = 8.9, 3.3 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.9, 153.9, 151.5, 123.2, 119.2, 114.8, 113.2, 56.6, 55.7, 51.0, 28.9. HRMS (ESI$^+$): calcd for $C_{13}H_{19}NO_3Na$ $[M+Na]^+$ 260.12626, found 260.12507.



***N*-(*tert*-butyl)-1-naphthamide (1r)**

The title compound was prepared according the **General procedure B**

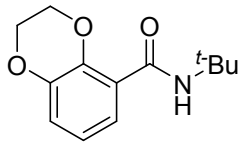
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 8.2 Hz, 2H), 7.58–7.49 (m, 3H), 7.43 (t, J = 7.6 Hz, 1H), 5.82 (brs, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.2, 136.0, 133.7, 130.07, 130.05, 128.3, 127.0, 126.3, 125.4, 124.8, 124.5, 52.1, 28.9. Spectroscopic data are in accordance with those described in the literature.[7]



***N*-(*tert*-butyl)benzo[d][1,3]dioxole-4-carboxamide (1s)**

The title compound was prepared according the **General procedure B**

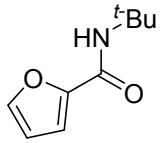
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57–7.50 (m, 1H), 6.92 (s, 1H), 6.91 (d, J = 1.8 Hz, 1H), 6.88 (brs, 1H), 6.06 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 147.3, 144.6, 122.2, 121.8, 117.1, 111.1, 101.2, 51.4, 28.8. HRMS (ESI$^+$): calcd for $C_{12}H_{15}NO_3Na$ $[M+Na]^+$ 244.09496, found 244.09373.



***N*-(*tert*-butyl)-2,3-dihydrobenzo[b][1,4]dioxine-5-carboxamide (1t)**

The title compound was prepared according the **General procedure B**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (dd, J = 7.7, 1.5 Hz, 1H), 7.50 (brs, 1H), 6.98–6.86 (m, 2H), 4.41–4.36 (m, 2H), 4.31–4.26 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.6, 143.4, 141.7, 123.7, 123.3, 121.2, 120.3, 64.8, 63.5, 51.1, 28.9. HRMS (ESI$^+$): calcd for $C_{13}H_{17}NO_3Na$ $[M+Na]^+$ 258.11061, found 258.10944.

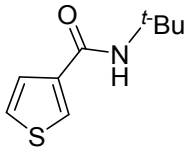


***N*-(*tert*-butyl)furan-2-carboxamide (1u)**

The title compound was prepared according the **General procedure A**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 0.9 Hz, 1H), 7.04 (d, J = 3.1 Hz, 1H), 6.46 (dd, J = 3.4, 1.7 Hz, 1H), 6.19 (brs, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz,

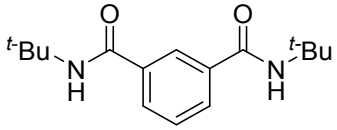
$CDCl_3$) δ = 157.8, 148.8, 143.2, 113.4, 112.1, 51.4, 28.9. HRMS (ESI^+): calcd for $C_9H_{13}NO_2Na$ $[M+Na]^+$ 190.08440, found 190.08334.



***N*-(*tert*-butyl)thiophene-3-carboxamide (1v)**

The title compound was prepared according the **General procedure A**

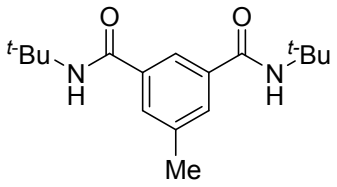
^1H NMR (400 MHz, $CDCl_3$) δ = 7.76 (s, 1H), 7.29 (dd, J = 19.0, 4.8 Hz, 2H), 5.89 (brs, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 138.8, 127.4, 126.2, 126.0, 51.5, 28.8. Spectroscopic data are in accordance with those described in the literature.[1]



***N*^{1},*N*^{3}-di-*tert*-butylisophthalamide (1w)**

The title compound was prepared according the **General procedure A**

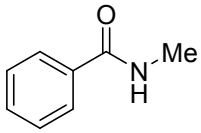
^1H NMR (400 MHz, $CDCl_3$) δ = 8.09 (t, J = 1.6 Hz, 1H), 7.83 (dd, J = 7.7, 1.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 6.08 (brs, 2H), 1.47 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.0, 135.9, 129.3, 128.7, 124.9, 51.9, 28.8. Spectroscopic data are in accordance with those described in the literature.[8]



***N*^{1},*N*^{3}-di-*tert*-butyl-5-methylisophthalamide (1x)**

The title compound was prepared according the **General procedure B**

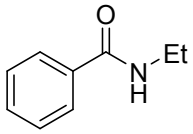
^1H NMR (400 MHz, $CDCl_3$) δ = 7.85 (s, 1H), 7.62 (s, 2H), 6.08 (brs, 2H), 2.40 (s, 3H), 1.46 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 138.7, 135.9, 130.0, 122.1, 51.8, 28.8, 21.3. HRMS (ESI^+): calcd for $C_{17}H_{26}N_2O_2Na$ $[M+Na]^+$ 313.18920, found 313.18747.



***N*-methylbenzamide (1y)**

The title compound was prepared according the **General procedure A**

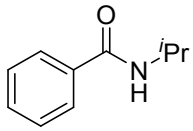
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81–7.72 (m, 2H), 7.50–7.42 (m, 1H), 7.42–7.34 (m, 2H), 6.48 (brs, 1H), 3.01–2.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.4, 134.6, 131.4, 128.5, 126.9, 26.9. Spectroscopic data are in accordance with those described in the literature.[9]



***N*-ethylbenzamide (1z)**

The title compound was prepared according the **General procedure A**

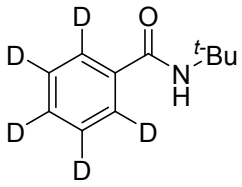
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79–7.73 (m, 2H), 7.51–7.45 (m, 1H), 7.45–7.38 (m, 2H), 6.18 (brs, 1H), 3.54–3.46 (m, 2H), 1.25 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.4, 134.8, 131.3, 128.5, 126. 8, 34.9, 14.9. Spectroscopic data are in accordance with those described in the literature.[9]



***N*-isopropylbenzamide (1aa)**

The title compound was prepared according the **General procedure A**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77–7.72 (m, 2H), 7.48–7.43 (m, 1H), 7.42–7.36 (m, 2H), 6.10 (brs, 1H), 4.34–4.22 (m, 1H), 1.24 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 134.9, 131.2, 128.4, 126.8, 41.8, 22.8. Spectroscopic data are in accordance with those described in the literature.[8]



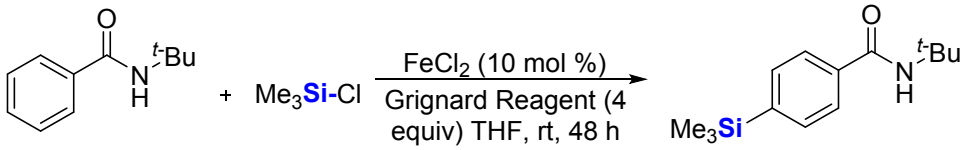
***N*-(*tert*-butyl)benzamide-2,3,4,5,6-d_5 (1a-d_5)**

The title compound was prepared according the **General procedure B**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.96 (brs, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.9, 135.8, 130.8, 130.5, 130.3, 128.2, 127.9, 127.7, 126.5, 126.3, 126.0, 51.6, 28.9. HRMS (ESI$^+$): calcd for $C_{11}H_{10}NOD_5Na$ $[M+Na]^+$ 205.13652, found 205.13536.

3. Optimizing Reaction Parameters

***Table S1.* Investigation of the Effect of the Amount of Grignard Reagent on Fe-Catalyzed *para*-Selective Formation of Silylation by Benzamide Derivatives[a]**

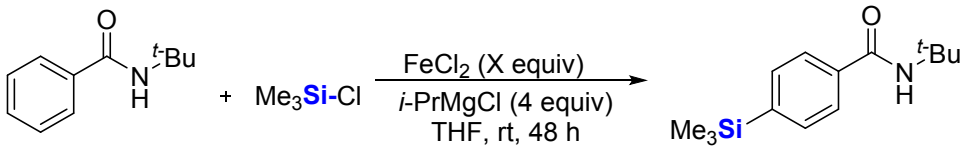


1 **2** **3**

Entry	Grignard Reagent	Yield (3)[b]
1	--	0
2	*i*-PrMgCl	74
3	*i*-BuMgCl	10
4	PhMgBr	ND
5	CyMgCl	ND
6	*t*-BuMgCl	10

[a]Conditions: **1** (0.2 mmol), **2** (0.6 mmol), $FeCl_2$ (0.02 mmol), grignard reagent (0.8 mmol), and THF (0.5 mL), under Ar atmosphere at rt for 48 h. [b]Isolated yield are shown. ND, not detected.

***Table S2.* Investigation of the Effect of the Amount of $FeCl_2$ on Fe-Catalyzed *para*-Selective Formation of Silylation by Benzamide Derivatives[a]**



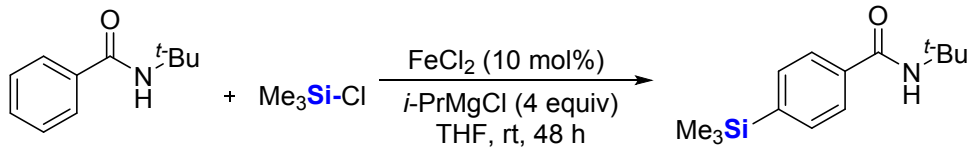
1 **2** **3**

Entry	$FeCl_2$ (X equiv)	Yield (3)[b]
1	0.05 equiv	50
2	0.1 equiv	74

3	0.15 equiv	70
4	0.2 equiv	65

[a]Conditions: **1** (0.2 mmol), **2** (0.6 mmol), $FeCl_2$ (0.05–0.2 equiv), *i*-PrMgCl (0.8 mmol), and THF (0.5 mL), under Ar atmosphere at rt for 48 h. [b]Isolated yield are shown. ND, not detected.

Table S3. **Investigation of the Effect of the Amount of TMS-Cl on Fe-Catalyzed *para*-Selective Formation of Silylation by Benzamide Derivatives[a]**



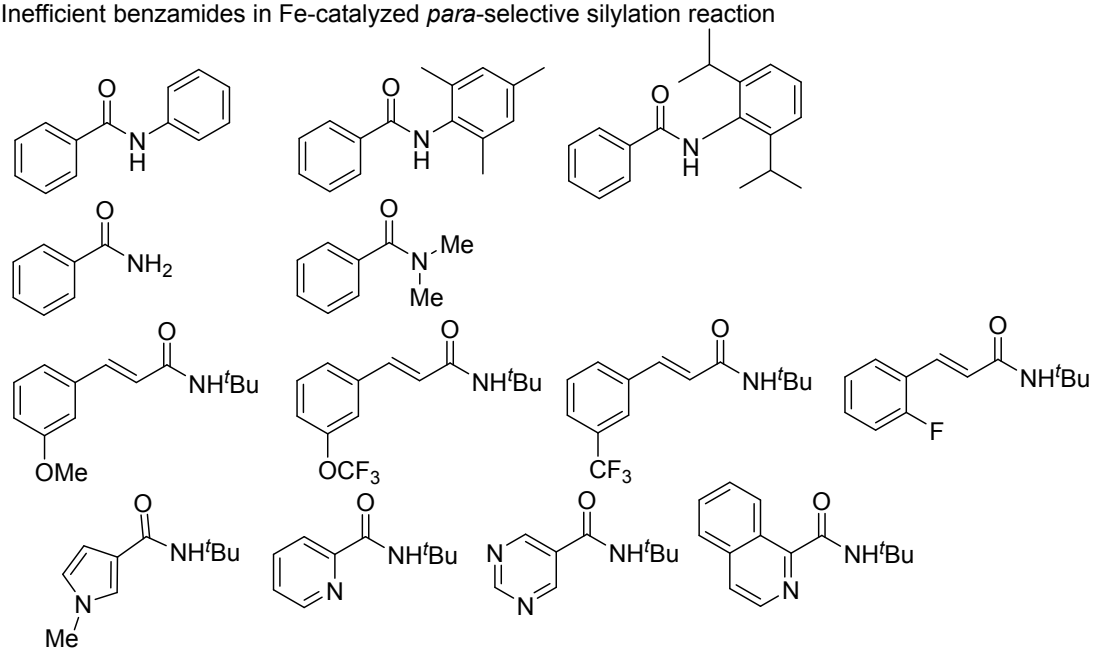
1 **2** **3**

Entry	Me_3Si-Cl (X equiv)	Yield (3a)[b]
1	1.0 equiv	10
2	2.0 equiv	40
3	3.0 equiv	74
4	4.0 equiv	72

[a]Conditions: **1** (0.2 mmol), **2** (1.0–4.0 equiv), $FeCl_2$ (0.02 mmol), *i*-PrMgCl (0.8 mmol), and THF (0.5 mL), under Ar atmosphere at rt for 48 h. [b]Isolated yield are shown. ND, not detected.

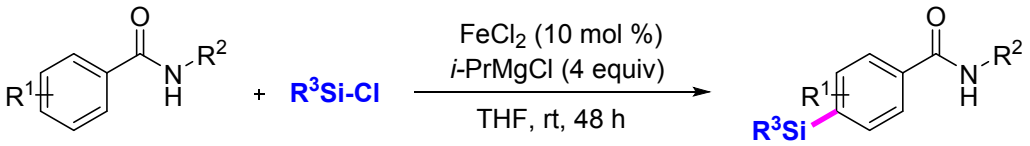
Table S4. **Inefficient benzamides and silylation reagents in Fe-catalyzed para-selective silylation reaction**

Inefficient benzamides in Fe-catalyzed *para*-selective silylation reaction

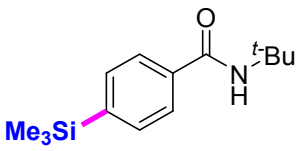


Et_3SiCl **t-$BuMe_2SiCl$** **i-Pr_3SiCl** **$Ph_2MeSiCl$** **···**

4. General Procedure for Fe-Catalyzed *para*-Selective Formation of Silylation by Benzamide Derivatives

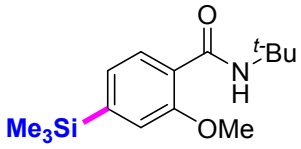


A dried Schlenk tube were placed *N*-(*tert*-butyl)benzamide **1** (0.2 mmol), $FeCl_2$ (0.02 mmol) and freshly distilled THF (0.5 mL). *i*-PrMgCl (0.8–1 mmol) was dropwise added by syringe at room temperature. After stirring the mixture for 30 min, chlorosilane (0.6 mmol) was added by syringe and the mixture was stirred at room temperature for 48 h. The resulting mixture was then quenched by an aqueous solution of NH_4Cl and extraction with ethyl acetate (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography to give the *para*-selective silylation product **3**.



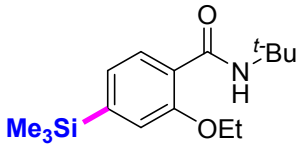
***N*-(*tert*-butyl)-4-(trimethylsilyl)benzamide (3)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 5.96 (brs, 1H), 1.46 (s, 9H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 144.4, 136.1, 133.5, 125.8, 51.6, 28.9, -1.3. HRMS (ESI$^+$): calcd for $C_{14}H_{24}NOSi$ $[M+H]^+$ 250.16272, found 250.16160. Spectroscopic data are in accordance with those described in the literature.[10]



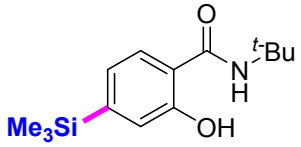
***N*-(*tert*-butyl)-2-methoxy-4-(trimethylsilyl)benzamide (4)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, J = 7.6 Hz, 1H), 7.86 (brs, 1H), 7.21 (dd, J = 7.6, 0.5 Hz, 1H), 7.05 (s, 1H), 3.96 (s, 3H), 1.45 (s, 9H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 156.4, 146.2, 131.0, 126.3, 123.0, 115.6, 55.8, 50.9, 28.9, -1.3. HRMS (ESI$^+$): calcd for $C_{15}H_{26}NO_2Si$ $[M+H]^+$ 280.17328, found 280.17197.



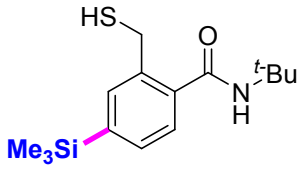
***N*-(*tert*-butyl)-2-ethoxy-4-(trimethylsilyl)benzamide (5)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.02 (brs, 1H), 4.20 (q, J = 6.9 Hz, 2H), 1.52 (t, J = 6.9 Hz, 3H), 1.45 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 156.0, 146.1, 130.9, 126.1, 122.9, 116.5, 64.6, 51.0, 28.9, 14.9, -1.3. HRMS (ESI$^+$): calcd for $C_{16}H_{28}NO_2Si$ $[M+H]^+$ 294.18893, found 294.18771.



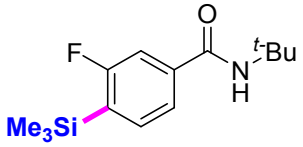
***N*-(*tert*-butyl)-2-hydroxy-4-(trimethylsilyl)benzamide (6)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (dd, J = 7.1, 1.8 Hz, 1H), 7.41–7.31 (m, 3H), 5.72 (brs, 1H), 1.47 (s, 9H), 0.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 143.7, 139.5, 135.3, 129.1, 128.6, 126.2, 51.6, 28.9, 0.2. HRMS (ESI$^-$): calcd for $C_{14}H_{22}NO_2Si$ $[M-H]^-$ 264.14198, found 264.14001.



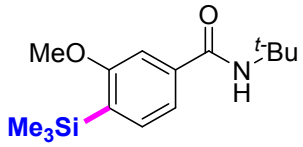
***N*-(*tert*-butyl)-2-(mercaptomethyl)-4-(trimethylsilyl)benzamide (7)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.2 (m, 1H), 7.04 (dd, J = 14.5, 7.5 Hz, 2H), 5.56 (brs, 1H), 2.41 (s, 2H), 1.45 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.9, 139.1, 136.2, 129.9, 129.1, 127.0, 123.8, 51.6, 28.8, 23.4, -1.4. HRMS (ESI$^+$): calcd for $C_{15}H_{26}NOSSi$ $[M+H]^+$ 296.15044, found 296.14993.



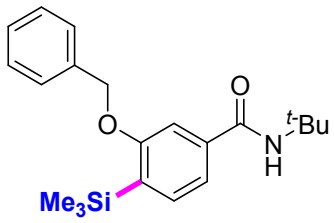
***N*-(*tert*-butyl)-3-fluoro-4-(trimethylsilyl)benzamide (8)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44–7.38 (m, 2H), 7.32 (d, J = 8.9 Hz, 1H), 5.94 (brs, 1H), 1.46 (s, 9H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.2 (d, J=241.0 Hz) , 165.7 (d, J=3.0 Hz), 139.1 (d, J = 7.0 Hz), 135.2 (d, J = 11.0 Hz), 130.0 (d, J=34.5 Hz), 121.7 (d, J = 3.0 Hz), 113.1 (d, 14.0 Hz), 51.7 , 28.7, -1.3 (d, 4.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -100.0. HRMS (ESI$^+$): calcd for $C_{14}H_{23}NOFSi$ $[M+H]^+$ 268.15329, found 268.15206.



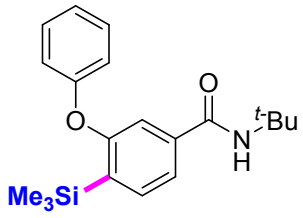
***N*-(*tert*-butyl)-3-methoxy-4-(trimethylsilyl)benzamide (9)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 1.2 Hz, 1H), 7.13 (dd, J = 7.4, 1.3 Hz, 1H), 6.01 (brs, 1H), 3.84 (s, 3H), 1.46 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.9, 164.6, 138.3, 134.7, 131.8, 117.4, 108.3, 55.13, 51.5, 28.8, -1.2. HRMS (ESI$^+$): calcd for $C_{15}H_{26}NO_2Si$ $[M+H]^+$ 280.17328, found 280.17192.



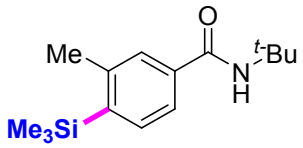
3-(benzyloxy)-*N*-(*tert*-butyl)-4-(trimethylsilyl)benzamide (10)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46–7.37(m, 6H), 7.33 (dd, J = 8.3, 5.9 Hz, 1H), 7.18 (dd, J = 7.4, 1.0 Hz, 1H), 5.98 (brs, 1H), 5.12 (s, 2H), 1.47 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.8, 163.7, 138.4, 136.7, 135.0, 132.0, 128.5, 127.9, 127.6, 117.7, 109.2, 70.0, 51.6, 28.8, -1.1. HRMS (ESI$^+$): calcd for $C_{21}H_{30}NO_2Si$ $[M+H]^+$ 356.20458, found 356.30312.



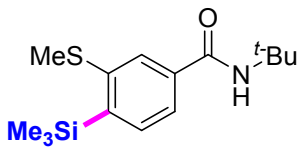
***N*-(*tert*-butyl)-3-phenoxy-4-(trimethylsilyl)benzamide (11)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, J = 7.6 Hz, 1H), 7.37–7.31 (m, 3H), 7.19 (d, J = 1.4 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.99–6.94 (m, 2H), 5.89 (s, 1H), 1.41 (s, 9H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.3, 162.2, 156.9, 138.5, 135.4, 134.4, 129.9, 123.3, 120.5, 118.8, 115.6, 51.6, 28.7, -1.1. HRMS (ESI$^+$): calcd for $C_{20}H_{28}NO_2Si$ $[M+H]^+$ 342.18893, found 342.18731.



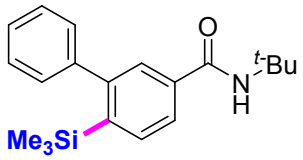
***N*-(*tert*-butyl)-3-methyl-4-(trimethylsilyl)benzamide (12)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (dd, J = 11.9, 8.6 Hz, 3H), 5.98 (brs, 1H), 2.48 (s, 3H), 1.46 (s, 9H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 143.8, 142.2, 136.3, 134.4, 127.7, 122.7, 51.5, 28.8, 22.9, -0.4. HRMS (ESI$^+$): calcd for $C_{15}H_{26}NOSi$ $[M+H]^+$ 264.17837, found 264.17700.



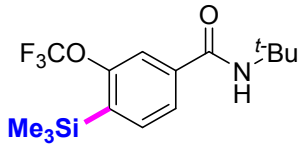
***N*-(*tert*-butyl)-3-(methylthio)-4-(trimethylsilyl)benzamide (13)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 1.3 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.33 (dd, J = 7.6, 1.5 Hz, 1H), 5.99 (brs, 1H), 2.50 (s, 3H), 1.45 (s, 9H), 0.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 145.9, 143.1, 136.9, 134.5, 125.1, 121.9, 51.61, 28.8, 17.4, -0.4. HRMS (ESI$^+$): calcd for $C_{15}H_{26}NOSSi$ $[M+H]^+$ 296.15044, found 296.14896.



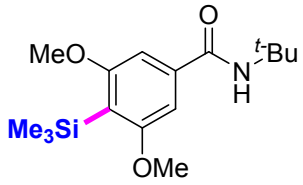
***N*-(*tert*-butyl)-6-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (14)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (dd, J = 7.8, 1.8 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 1.5 Hz, 1H), 7.42–7.35 (m, 3H), 7.28 (dd, J = 6.5, 3.1 Hz, 2H), 5.99 (brs, 1H), 1.46 (s, 9H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7, 149.3, 143.6, 142.3, 135.7, 134.9, 129.3, 127.7, 127.4, 127.1, 124.5, 51.6, 28.8, 0.3. HRMS (ESI$^+$): calcd for $C_{20}H_{28}NOSi$ $[M+H]^+$ 326.19402, found 326.19248.



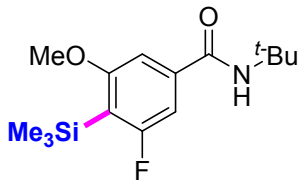
***N*-(*tert*-butyl)-3-(trifluoromethoxy)-4-(trimethylsilyl)benzamide (15)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.49 (s, 2H), 5.97 (brs, 1H), 1.46 (s, 9H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.5, 154.6, 138.7, 135.6, 135.4, 123.3, 116.5, 51.8, 29.7, 28.7, -1.1;^{19}F NMR (470 MHz, $CDCl_3$) δ -55.8. HRMS (ESI$^+$): calcd for $C_{15}H_{23}NO_2F_3Si$ $[M+H]^+$ 334.14502, found 334.14343.



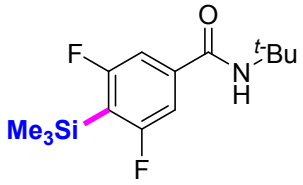
***N*-(*tert*-butyl)-3,5-dimethoxy-4-(trimethylsilyl)benzamide (16)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.79 (s, 2H), 5.99 (brs, 1H), 3.77 (s, 6H), 1.46 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 165.3, 139.1, 117.8, 101.8, 55.3, 51.6, 28.8, 1.1. HRMS (ESI$^+$): calcd for $C_{16}H_{28}NO_3Si$ $[M+H]^+$ 310.18385, found 310.18236.



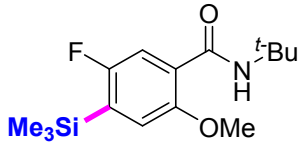
***N*-(*tert*-butyl)-3-fluoro-5-methoxy-4-(trimethylsilyl)benzamide (17)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (d, J = 0.9 Hz, 1H), 6.79 (dd, J = 9.0, 1.1 Hz, 1H), 5.99 (brs, 1H), 3.80 (s, 3H), 1.44 (s, 9H), 0.29 (d, J = 1.9 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0 (d, J = 243.0 Hz), 165.8 (d, J = 5.0 Hz), 165.5 (d, J = 16.0 Hz), 139.5 (d, J = 9.0 Hz), 117.0 (d, J = 32 Hz), 105.7 (d, J = 30.0 Hz), 104.6 (d, J = 2.0 Hz), 55.5, 51.7, 28.7, 0.3 (d, J = 16.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ = -98.0. HRMS (ESI$^+$): calcd for $C_{15}H_{25}NO_2FSi$ $[M+H]^+$ 298.16386, found 298.16243.



***N*-(*tert*-butyl)-3,5-difluoro-4-(trimethylsilyl)benzamide (18)**

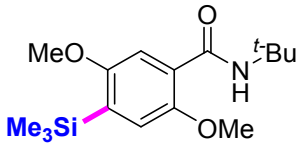
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13–7.08 (m, 2H), 5.94 (brs, 1H), 1.44 (s, 9H), 0.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1 (d, J = 15.0 Hz), 165.7 (d, J = 16.0 Hz), 164.5 (t, J = 3.0 Hz), 140.1 (t, J = 9.0 Hz), 116.9 (t, J = 34.0 Hz), 109.6 (d, J = 2.0 Hz), 109.3 (d, J = 2.0 Hz), 51.9, 28.7, 0.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -96.0. HRMS (ESI$^+$): calcd for $C_{14}H_{22}NOF_2Si$ $[M+H]^+$ 286.14387, found 286.14270.



***N*-(*tert*-butyl)-5-fluoro-2-methoxy-4-(trimethylsilyl)benzamide (19)**

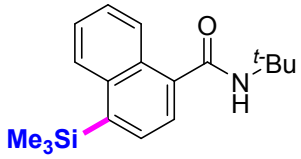
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (brs, 1H), 7.77 (d, J = 9.1 Hz, 1H), 6.89 (d, J = 3.9 Hz, 1H), 3.94 (s, 3H), 1.44 (s, 9H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =

163.0, 161.9 (d, J = 232.0 Hz), 152.9 (d, J = 2.0 Hz), 131.0 (d, J = 33.0 Hz), 125.5 (d, J = 8.0 Hz), 117.5 (d, J = 11.0 Hz), 117.4 (d, J = 30.0 Hz), 56.6, 51.1, 28.9, -1.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -110.0. HRMS (ESI$^+$): calcd for $C_{15}H_{25}NO_2FSi$ $[M+H]^+$ 298.16386, found 298.16254.



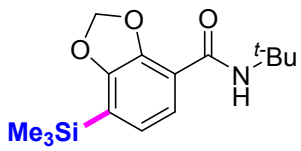
***N*-(*tert*-butyl)-2,5-dimethoxy-4-(trimethylsilyl)benzamide (20)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (brs, 1H), 7.66 (s, 1H), 6.95 (s, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 1.45 (s, 9H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 158.8, 151.1, 133.3, 124.1, 118.7, 111.9, 56.7, 55.7, 51.0, 28.9, -1.1. HRMS (ESI$^+$): calcd for $C_{16}H_{28}NO_3Si$ $[M+H]^+$ 310.18385, found 310.18221.



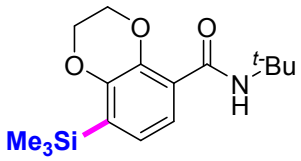
***N*-(*tert*-butyl)-4-(trimethylsilyl)-1-naphthamide (21)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31–8.25 (m, 1H), 8.15–8.09 (m, 1H), 7.65 (d, J = 6.9 Hz, 1H), 7.57–7.51 (m, 2H), 7.48 (d, J = 6.9 Hz, 1H), 5.83 (brs, 1H), 1.53 (s, 9H), 0.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.3, 140.8, 137.3, 137.0, 132.0, 129.7, 128.4, 126.3, 126.2, 125.9, 123.2, 52.0, 28.8, 0.1. HRMS (ESI$^+$): calcd for $C_{18}H_{26}NOSi$ $[M+H]^+$ 300.17837, found 300.17688.



***N*-(*tert*-butyl)-7-(trimethylsilyl)benzo[d][1,3]dioxole-4-carboxamide (22)**

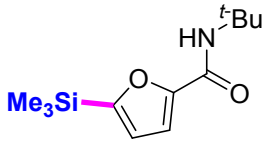
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.92 (brs, 1H), 6.04 (s, 2H), 1.45 (s, 9H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.6, 152.0, 143.1, 126.5, 123.0, 121.5, 117.4, 100.6, 51.4, 28.9, -1.5. HRMS (ESI$^+$): calcd for $C_{15}H_{24}NO_3Si$ $[M+H]^+$ 294.15255, found 294.15114.



***N*-(*tert*-butyl)-8-(trimethylsilyl)-2,3-dihydrobenzo[b][1,4]dioxine-5-carboxamide (23)**

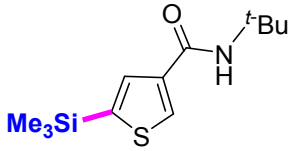
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, J = 7.7, 1.0 Hz, 1H), 7.54 (brs, 1H), 6.97 (dd, J = 7.7, 1.0 Hz, 1H), 4.40–4.35 (m, 2H), 4.30–4.26 (m, 2H), 1.43 (s, 9H), 0.25 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.8, 147.7, 140.8, 132.1, 126.2, 124.1, 123.1, 64.60, 63.2, 51.0, 28.8, -1.2. HRMS (ESI$^+$): calcd for $C_{16}H_{26}NO_3Si$ $[M+H]^+$ 308.16820, found 308.16680.



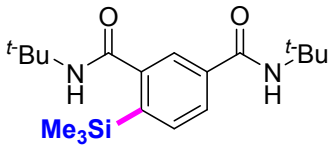
***N*-(*tert*-butyl)-5-(trimethylsilyl)furan-2-carboxamide (24)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, J = 1.4 Hz, 1H), 6.43 (d, J = 1.3 Hz, 1H), 6.24 (brs, 1H), 1.44 (s, 9H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 152.1, 141.9, 123.9, 117.0, 51.1, 28. 9, -1.0. HRMS (ESI$^+$): calcd for $C_{12}H_{21}NO_2NaSi$ $[M+Na]^+$ 262.12393, found 262.12292.



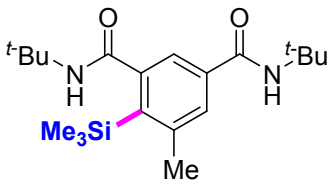
***N*-(*tert*-butyl)-5-(trimethylsilyl)thiophene-3-carboxamide (25)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, J = 4.8 Hz, 1H), 7.24 (d, J = 4.8 Hz, 1H), 5.68 (brs, 1H), 1.45 (s, 9H), 0.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7, 144.9, 144.2, 130.1, 127.3, 51.5, 28.8, 0.0. HRMS (ESI$^+$): calcd for $C_{12}H_{21}NOSNaSi$ $[M+Na]^+$ 278.10108, found 278.10008.



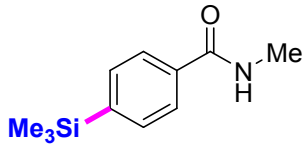
***N*^{1},*N*^{3}-di-*tert*-butyl-4-(trimethylsilyl)isophthalamide (26)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 6.00 (brs, 1H), 5.92 (brs, 1H), 1.46 (s, 18H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.9, 166.4, 144.1, 143.5, 135.7, 135.4, 126.0, 124.9, 51.8, 51.8, 28.8, 0.1. HRMS (ESI$^+$): calcd for $C_{19}H_{32}N_2O_2NaSi$ $[M+Na]^+$ 371.21307, found 371.21151.



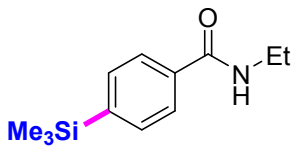
***N*^{1},*N*^{3}-di-*tert*-butyl-5-methyl-4-(trimethylsilyl)isophthalamide (27)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, J = 1.5 Hz, 1H), 7.36 (d, J = 1.4 Hz, 1H), 5.95 (brs, 1H), 5.76 (brs, 1H), 2.49 (s, 3H), 1.45 (d, J = 2.6 Hz, 18H), 0.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.0, 166.3, 146.4, 145.5, 140.8, 135.5, 128.5, 123.0, 51.94, 51.7, 28.8, 28.8, 24.5, 1.9. HRMS (ESI$^+$): calcd for $C_{20}H_{34}N_2O_2NaSi$ $[M+Na]^+$ 385.22872, found 385.22707.



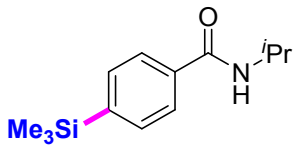
***N*-methyl-4-(trimethylsilyl)benzamide (28)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 7.9 Hz, 2H), 6.33 (brs, 1H), 3.00 (d, J = 4.8 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.3, 144.7, 134.7, 133.5, 125.9, 26.8, -1.3. HRMS (ESI$^+$): calcd for $C_{11}H_{18}NOSi$ $[M+H]^+$ 208.11577, found 208.11480.



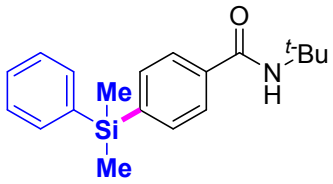
***N*-ethyl-4-(trimethylsilyl)benzamide (29)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 6.29 (brs, 1H), 3.52–3.45 (m, 2H), 1.23 (t, J = 7.3 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.5, 144.7, 134.9, 133.4, 125.9, 34.8, 14.9, -1.3. HRMS (ESI$^+$): calcd for $C_{12}H_{20}NOSi$ $[M+H]^+$ 222.13142, found 222.13038.



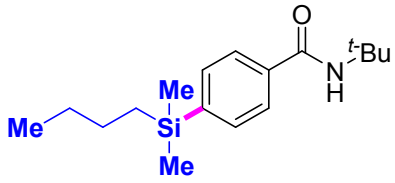
***N-iso*propyl-4-(trimethylsilyl)benzamide (30)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 6.11 (brs, 1H), 4.36–4.17 (m, 1H), 1.25 (s, 3H), 1.23 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7, 144.5, 135.0, 133.4, 125.9, 41.8, 22.8, -1.3. HRMS (ESI$^+$): calcd for $C_{13}H_{22}NOSi$ $[M+H]^+$ 236.14707, found 236.14587.



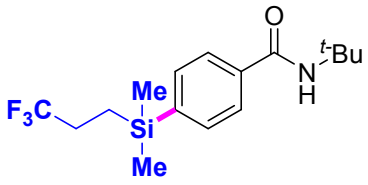
***N*-(*tert*-butyl)-4-(dimethyl(phenyl)silyl)benzamide (31)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.51 (dd, J = 7.4, 1.9 Hz, 2H), 7.40–7.33 (m, 3H), 6.03 (brs, 1H), 1.48 (s, 9H), 0.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 142.2, 137.6, 136.4, 134.4, 134.2, 129.4, 128.0, 125.9, 51.6, 28.9, -2.5. HRMS (ESI$^+$): calcd for $C_{19}H_{26}NOSi$ $[M+H]^+$ 312.17837, found 312.17693.



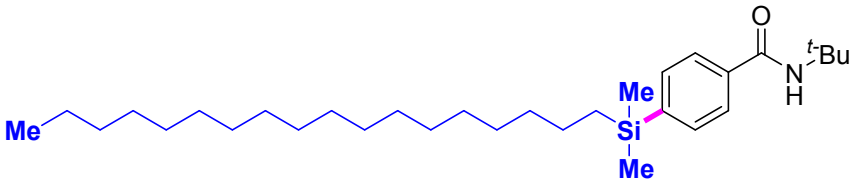
***N*-(*tert*-butyl)-4-(butyldimethylsilyl)benzamide (32)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 6.01 (brs, 1H), 1.46 (s, 9H), 1.33–1.23 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H), 0.73 (dd, J = 9.6, 6.7 Hz, 2H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 143.6, 135.9, 133.6, 125.7, 51.5, 28.8, 26.4, 25.9, 15.2, 13.7, -3.2. HRMS (ESI$^+$): calcd for $C_{17}H_{30}NOSi$ $[M+H]^+$ 292.20967, found 292.20824.



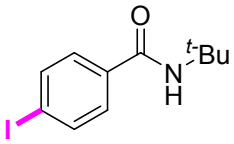
***N*-(*tert*-butyl)-4-(dimethyl(3,3,3-trifluoropropyl)silyl)benzamide (33)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 5.98 (brs, 1H), 2.00–1.91 (m, 2H), 1.47 (s, 9H), 0.99–0.93 (m, 2H), 0.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.8, 141.1, 136.7, 133.6, 128.7, 126.1, 51.6, 29.7, 28.8, 28.5, 7.4, -3.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ = -68.6. HRMS (ESI$^+$): calcd for $C_{16}H_{24}NOF_3SiNa$ $[M+H]^+$ 354.14770, found 354.14606.



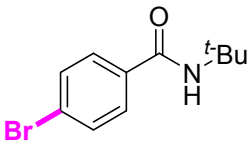
***N*-(*tert*-butyl)-4-(dimethyl(octadecyl)silyl)benzamide (34)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 5.95 (brs, 1H), 1.47 (s, 9H), 1.26 (d, J = 9.1 Hz, 32H), 0.88 (t, J = 6.8 Hz, 3H), 0.76–0.69 (m, 2H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 143.7, 136.0, 133.7, 125.7, 51.5, 33.6, 31.9, 29.68, 29.65, 29.6, 29.4, 29.3, 28.8, 23.8, 22.7, 15.5, 14.1, -3.1. HRMS (ESI$^+$): calcd for $C_{31}H_{58}NOSi$ $[M+H]^+$ 488.42877, found 488.42705.



***N*-(*tert*-butyl)-4-iodobenzamide (35)**

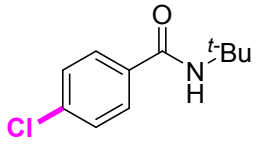
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.01 (brs, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.1, 137.5, 135.2, 128.3, 97.8, 51.7, 28.7. HRMS (ESI$^+$): calcd for $C_{11}H_{15}NOI$ $[M+H]^+$ 304.01983, found 304.01839.



4-bromo-*N*-(*tert*-butyl)benzamide (36)

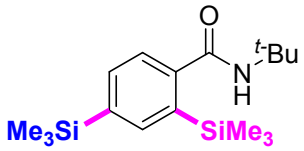
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.04 (brs, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.9, 134.6, 131.5,

128.3, 125.5, 51.7, 28.7. HRMS (ESI$^+$): calcd for $C_{11}H_{15}NOBr$ $[M+H]^+$ 256.03370, found 256.03257.



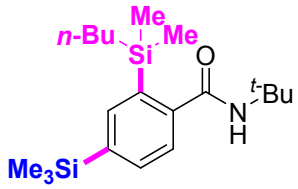
***N*-(*tert*-butyl)-4-chlorobenzamide (37)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.96 (brs, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.8, 137.1, 134.2, 128.6, 128.1, 51.7, 28.8. HRMS (ESI$^+$): calcd for $C_{11}H_{15}NOCl$ $[M+H]^+$ 212.08422, found 212.08320.



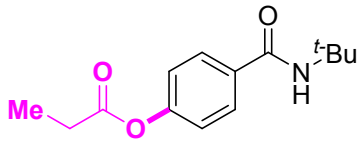
***N*-(*tert*-butyl)-2,4-bis(trimethylsilyl)benzamide (38)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (s, 1H), 7.52 (dd, J = 7.5, 1.1 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 5.74 (brs, 1H), 1.48 (s, 9H), 0.37 (s, 9H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 144.0, 141.6, 140.1, 138.1, 133.7, 125.3, 51.6, 28.8, 0.2, -1.3. HRMS (ESI$^+$): calcd for $C_{17}H_{31}NONaSi_2$ $[M+Na]^+$ 344.18419, found 344.18246.



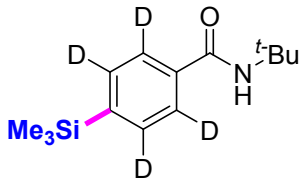
***N*-(*tert*-butyl)-2-(butyldimethylsilyl)-4-(trimethylsilyl)benzamide (39)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (s, 1H), 7.50 (dd, J = 7.5, 1.1 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 5.68 (brs, 1H), 1.46 (s, 9H), 1.37–1.28 (m, 4H), 0.88 (dd, J = 15.2, 8.3 Hz, 5H), 0.33 (s, 6H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 144.3, 141.4, 140.5, 137.2, 133.6, 125.4, 51.6, 28.9, 26.6, 26.5, 16.0, 13.9, -1.3, -1.6. HRMS (ESI$^+$): calcd for $C_{20}H_{37}NONaSi_2$ $[M+Na]^+$ 386.23114, found 386.22961.



4-(*tert*-butylcarbamoyl)phenyl propionate (40)

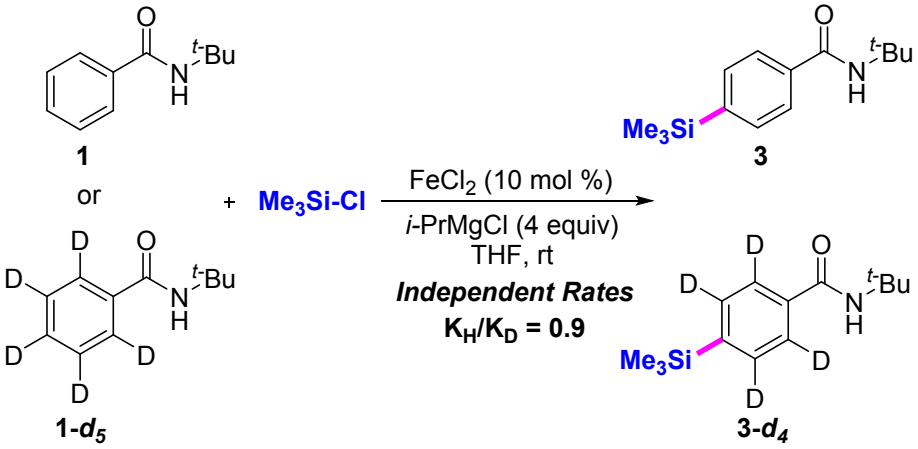
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 5.90 (brs, 1H), 2.60 (q, J = 7.5 Hz, 2H), 1.46 (s, 9H), 1.26 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.6, 166.1, 152.8, 133.4, 128.1, 121.6, 51.7, 28.8, 27.7, 8.9. HRMS (ESI$^+$): calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$250.14432, found 250.14398.

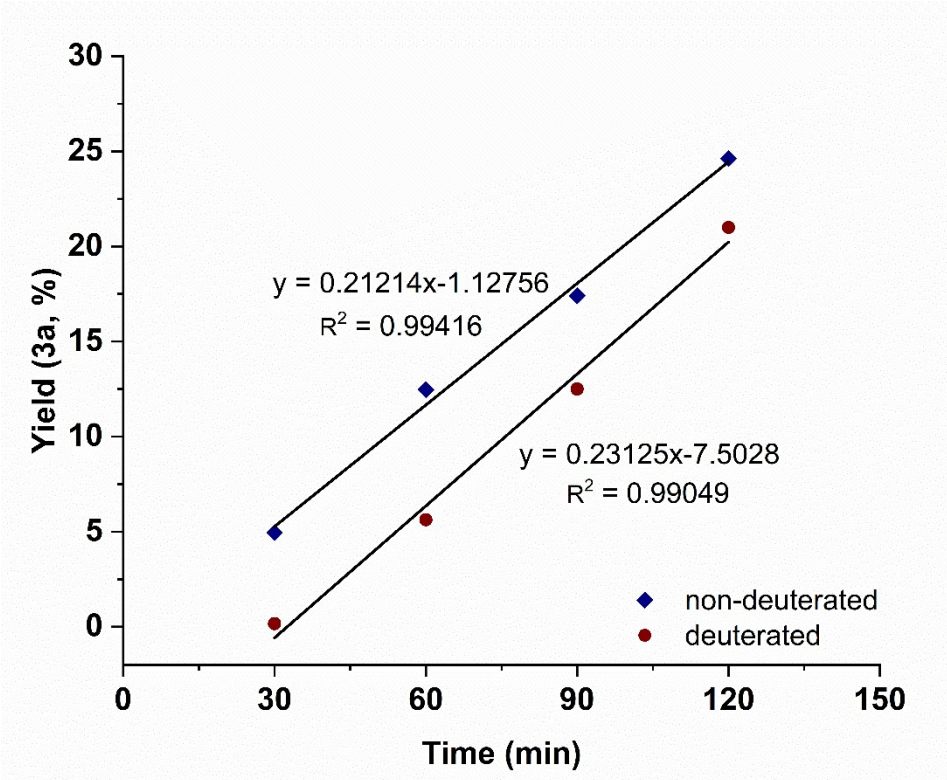


***N*-(*tert*-butyl)-4-(trimethylsilyl)benzamide-2,3,5,6-d_4 (3-d_4)**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.97 (brs, 1H), 1.46 (s, 9H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 144.2, 135.9, 133.2, 133.0, 132.8, 125.6, 125.3, 125.1, 51.6, 28.9, -1.3. HRMS (ESI$^+$): calcd for $C_{14}H_{20}D_4NOSi$ $[M+H]^+$254.18782, found 254.18.659.

5. Experiments of Kinetic Isotope Effect

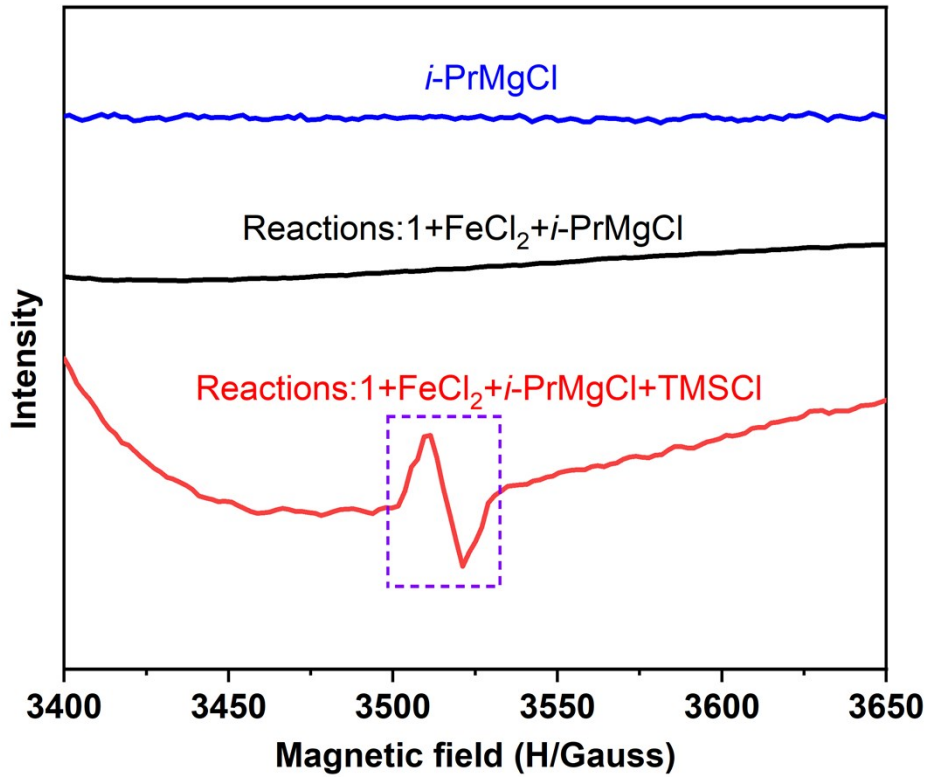


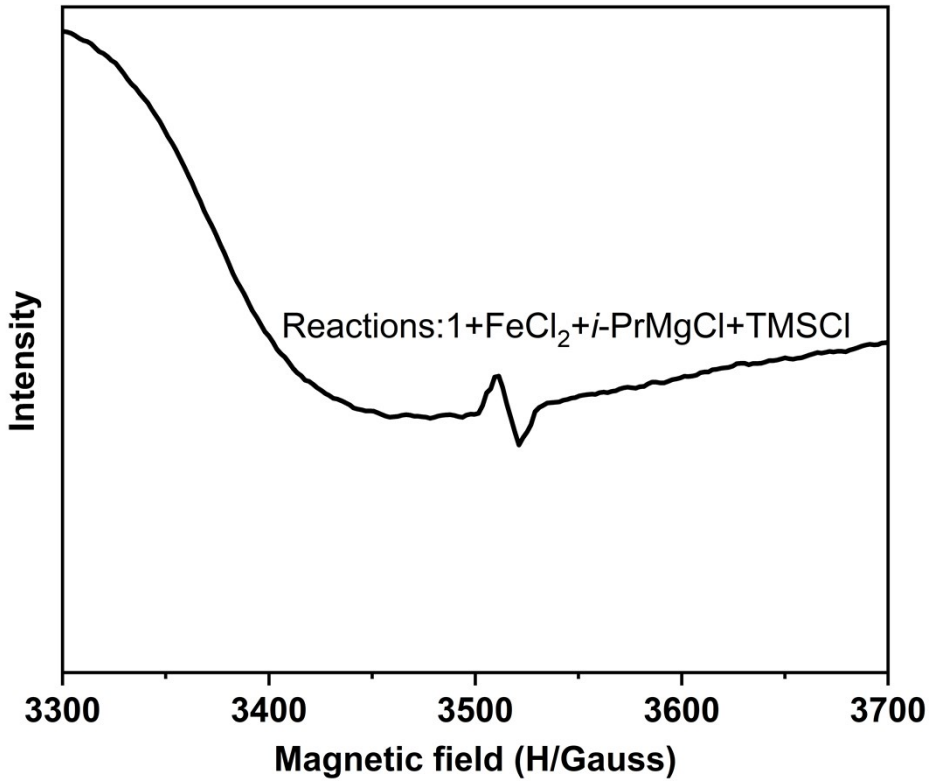


A dried Schlenk tube were placed *N*-(*tert*-butyl)benzamide **1** (0.2 mmol) or **1a-*d*$_5$** (0.2 mmol) and $FeCl_2$ (0.02 mmol) and freshly distilled THF (0.5 mL). *i*-PrMgCl (0.4 mL 0.8 mmol) was dropwise added by syringe at room temperature. After stirring the mixture for 30 min, TMSCl (0.6 mmol) was added by syringe and reacted then reacted for the designated time (30 min, 60 min, 90 min, 120 min) at room temperature. Then, the reaction mixture quenched with aqueous solution of NH_4Cl. The yield was determined by GC analysis. A value of $K_H/K_D = 0.9$ was obtained.

6. EPR studies of stoichiometric reactions

X-band EPR spectrum of the standard silylation after 3 hours was recorded at room temperature. The sharp peak at about 3500 Oe is typical for radicals with the *g* value around 2.0, indicating that radical species are involved in the silylation. Analysis of *iso*-propylmagnesium chloride in THF by EPR spectroscopy suggested that no radical species was existed in the solution.


i-PrMgCl
Reactions:1+FeCl2+i-PrMgCl
Reactions:1+FeCl2+i-PrMgCl+TMSCl
Intensity
3400
3450
3500
3550
3600
3650
Magnetic field (H/Gauss)


Reactions:1+FeCl2+i-PrMgCl+TMSCl
Intensity
3300
3400
3500
3600
3700
Magnetic field (H/Gauss)

7. Supplementary References

[1] H. Jiang, B. Liu, Y. Li, A. Wang, H. Huang, *Org. Lett.* **2011**, *13*, 1028-1031.

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[3] E. Bellamy, O. Bayh, C. Hoarau, F. Trécourt, G. Quéguiner, F. Marsais, *Chem. Commun.* **2010**, *46*, 7043-7045.

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[10] M. Tobisu, Y. Kita, Y. Ano, N. Chatani, *J. Am. Chem. Soc.* **2008**, *130*, 15982-15989.

8. X-Ray Crystal Structure of 3

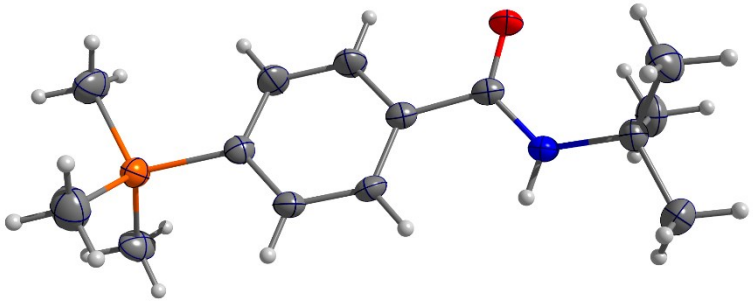
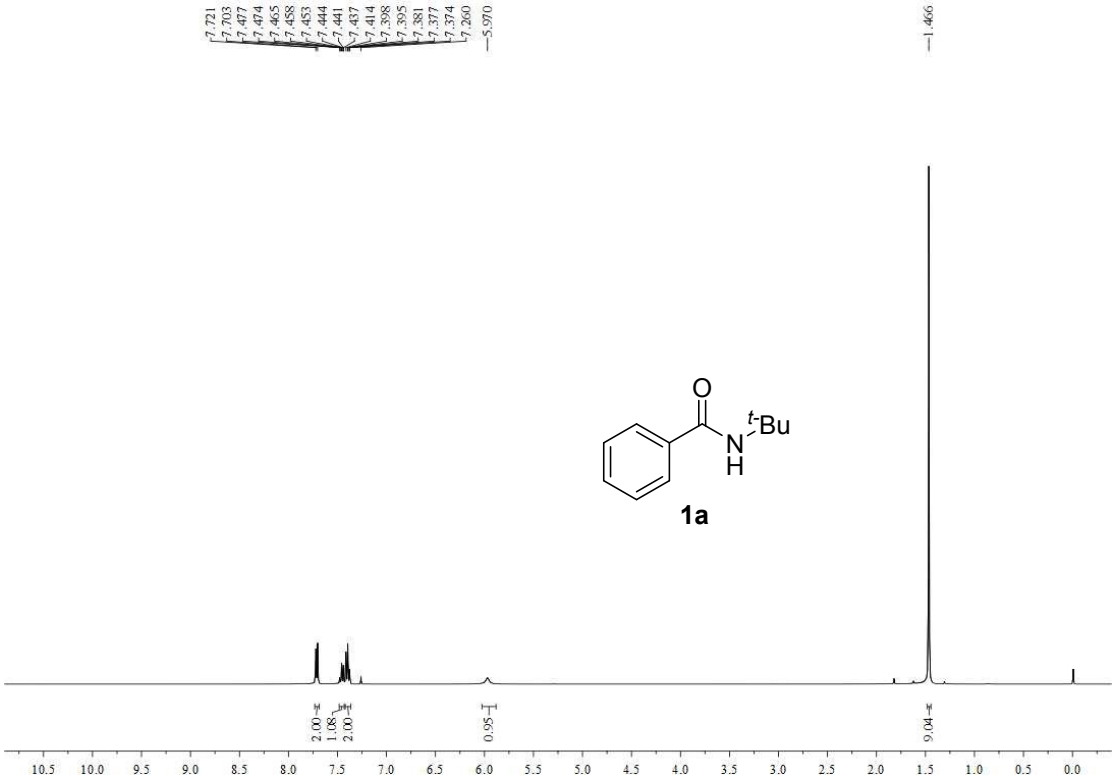


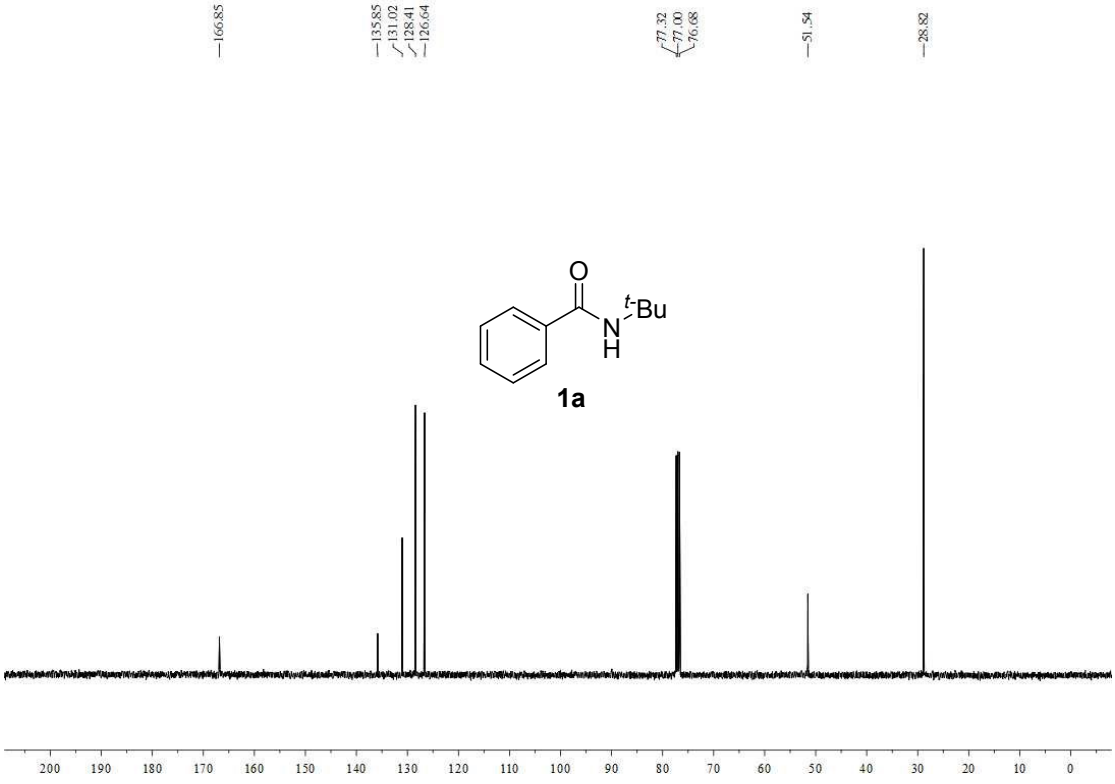
***Table S4*. Crystal data and structure refinement for 3**

Empirical formula	$C_{14}H_{23}NOSi$
Formula weight	249.42
Temperature	296.15 K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, *Pbca*
Unit cell dimensions	a = 10.2659(17) α/° 90
	b = 11.991(2) β/° 90
	c = 25.229(4) γ/° 90
Volume	3105.7(9)
Z, Calculated density	8, 1.067
Absorption coefficient	0.138 mm^-1
F(000)	1088.0
Crystal size	0.15 × 0.12 × 0.10
Theta range for data collection	3.228 to 53.234
Limiting indices	$-12 \le h \le 12$, $-15 \le k \le 15$, $-31 \le l \le 31$
Reflections collected	3245 [Rint = 0.0445, Rsigma = 0.0232]
Completeness to theta = 24.813	99.8 %

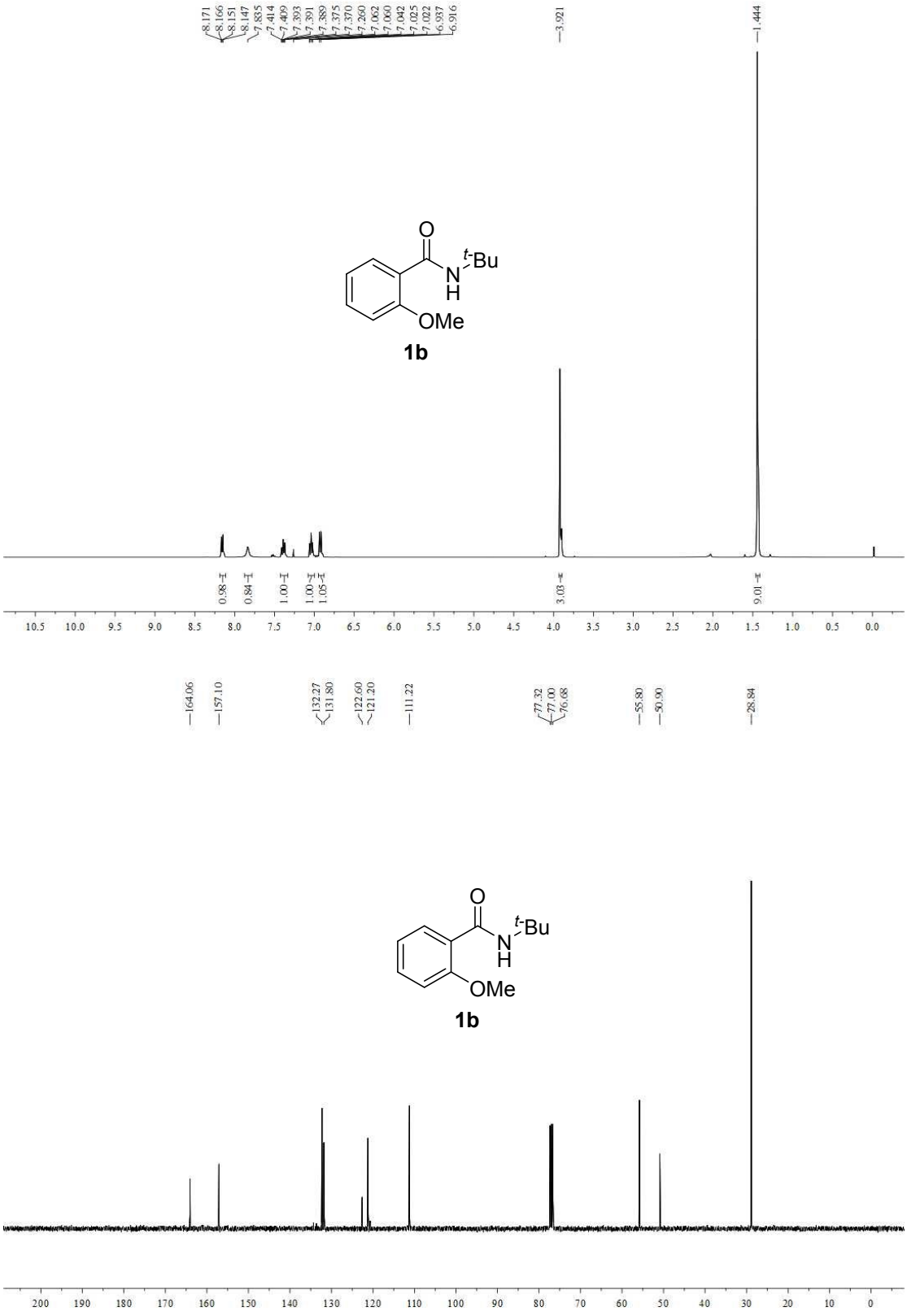
Data / restraints / parameters	3245 / 0 / 160
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0961
R indices (all data)	R1 = 0.0600, wR2 = 0.1093
Extinction coefficient	n/a
Largest diff. peak and hole	0.40/-0.18

9. ^{1}H, ^{13}C and ^{19}F NMR Spectra

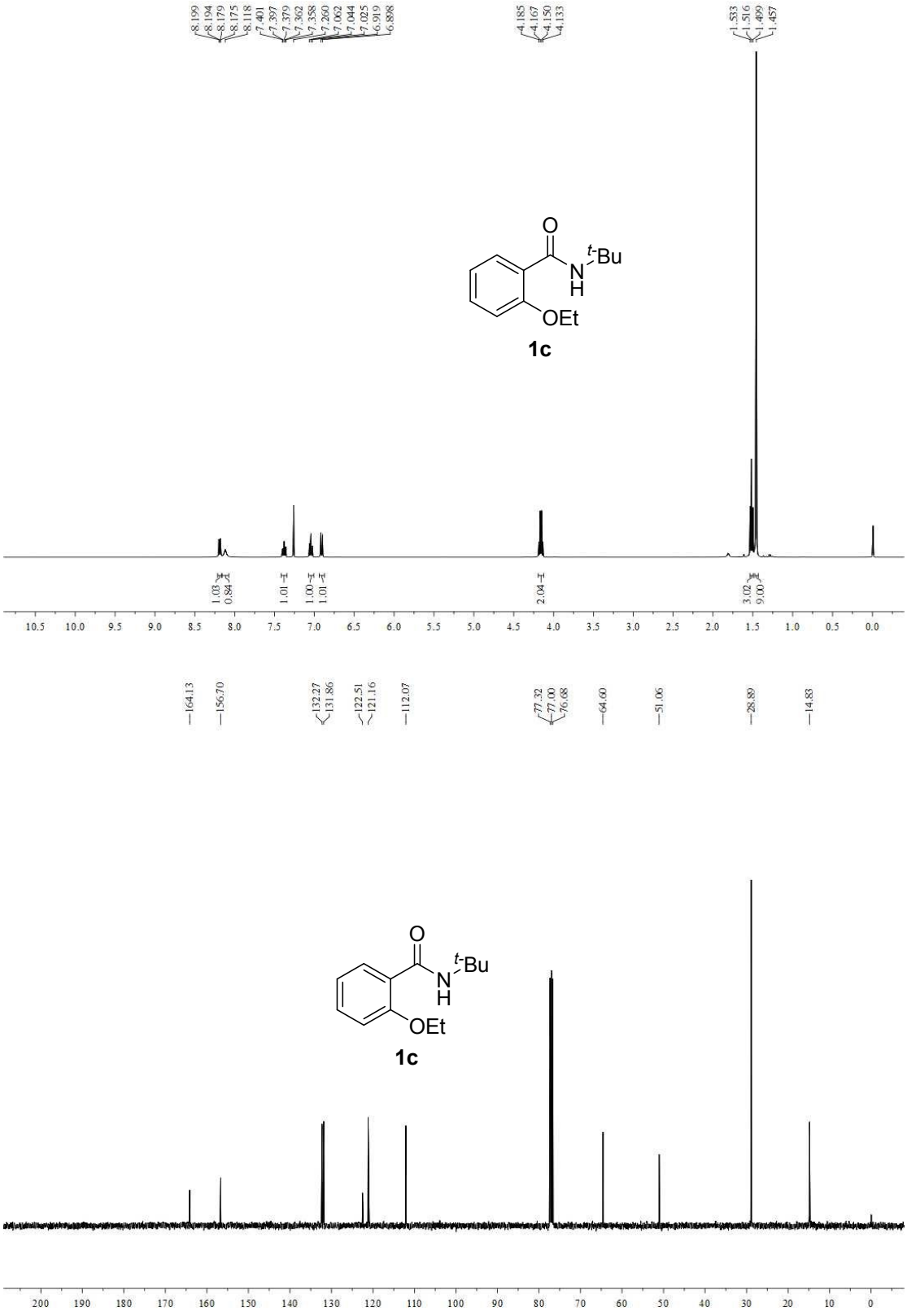




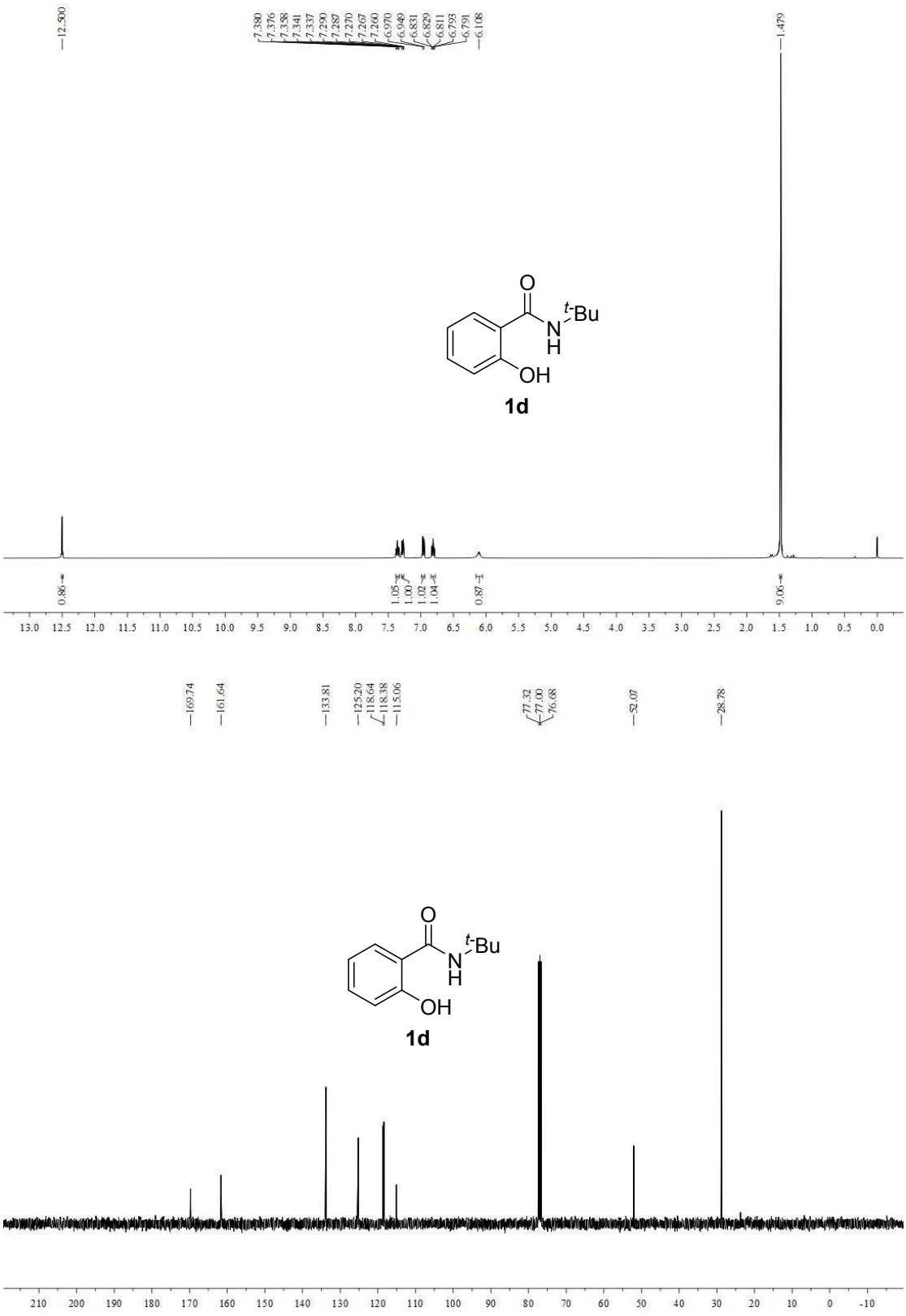
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1a



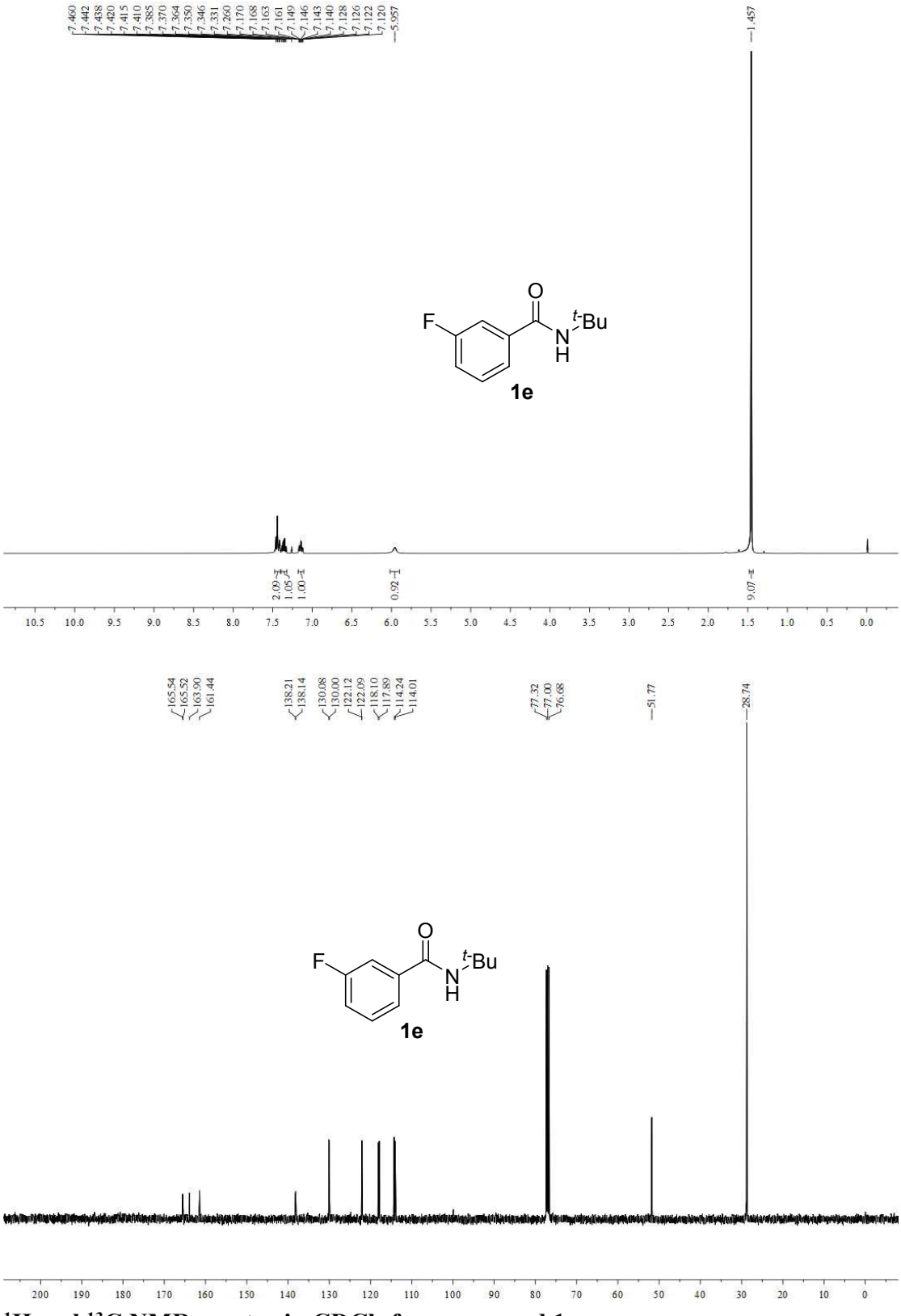
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1b



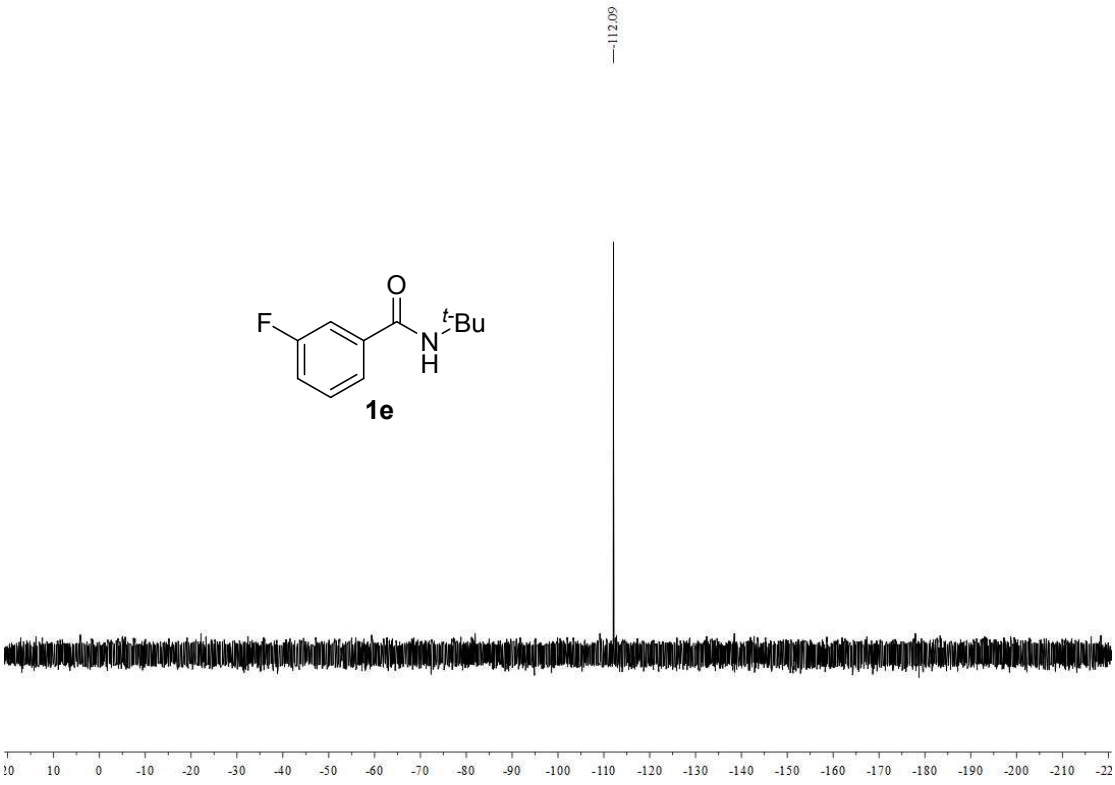
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1c



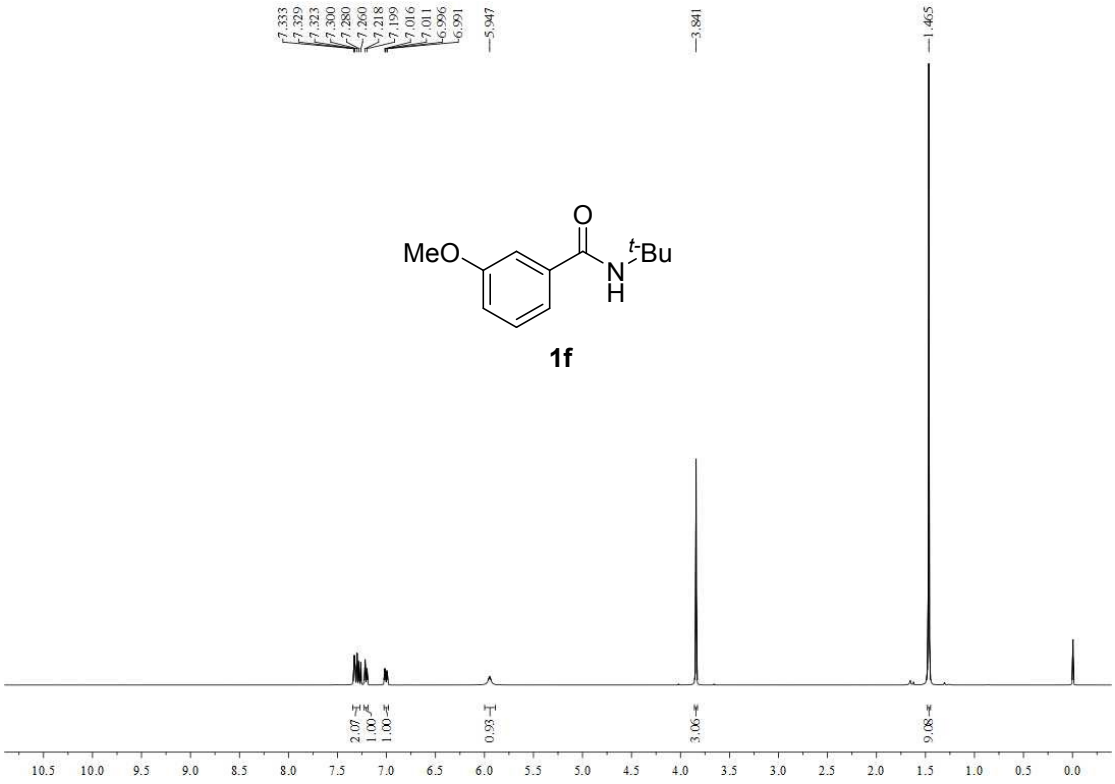
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1d

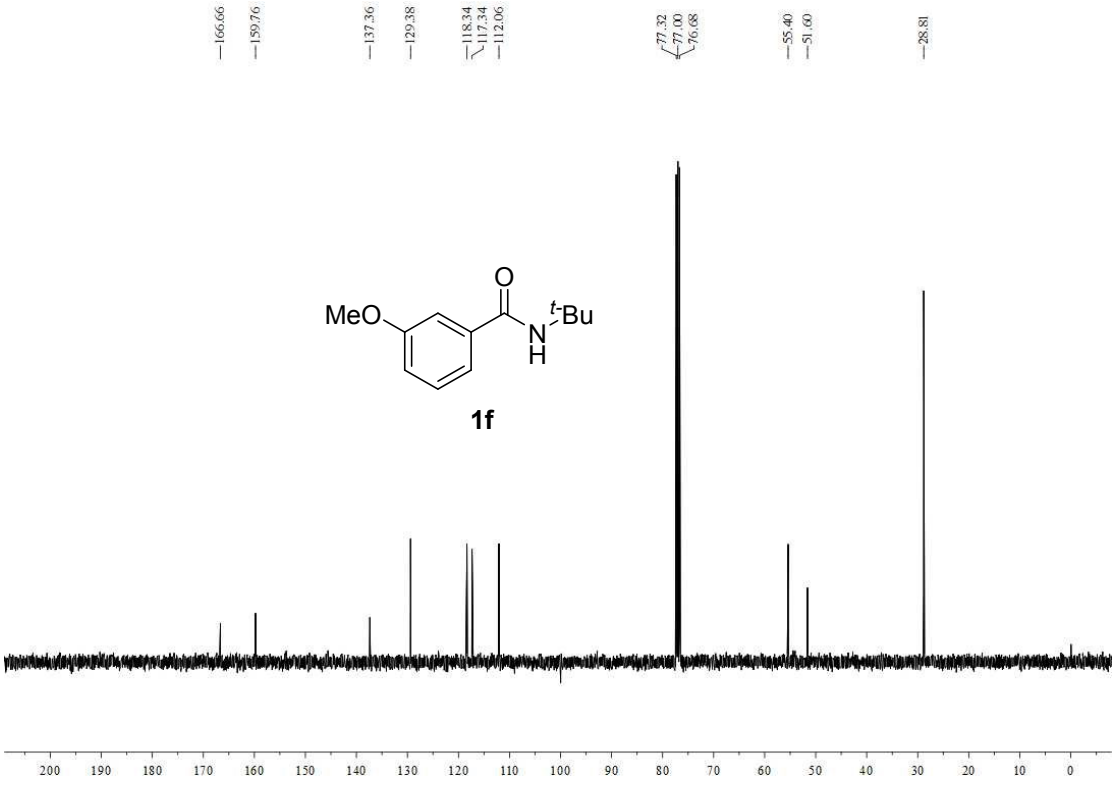


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1e

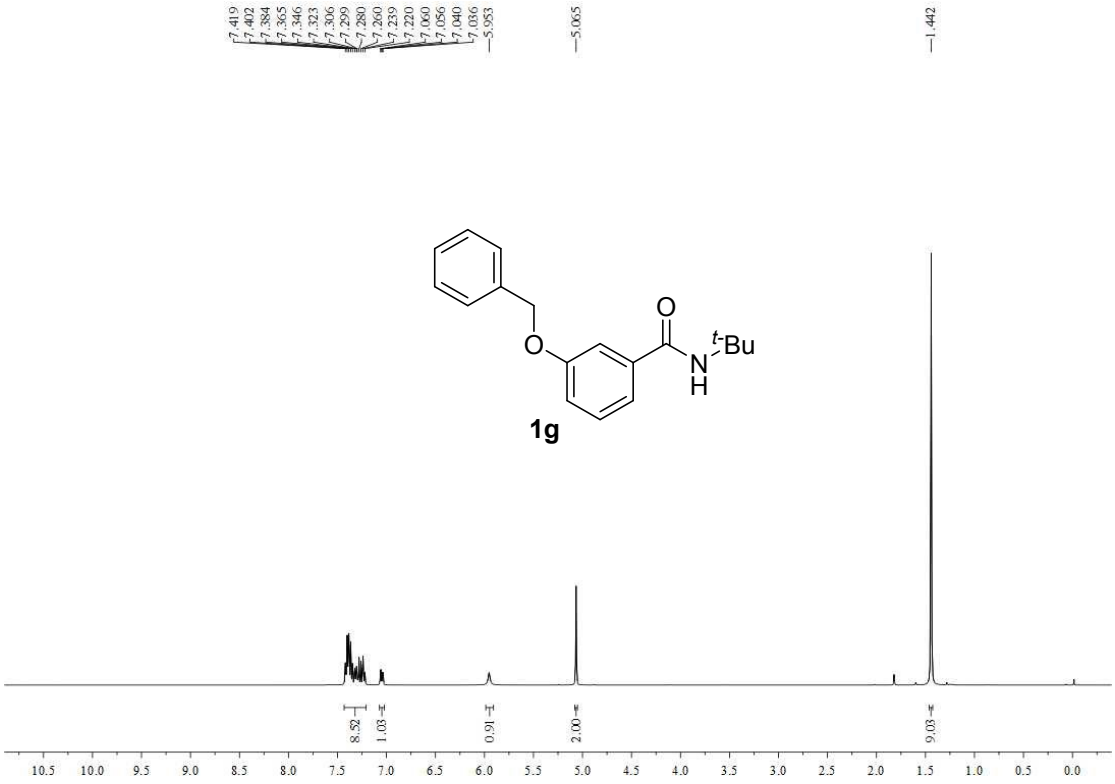


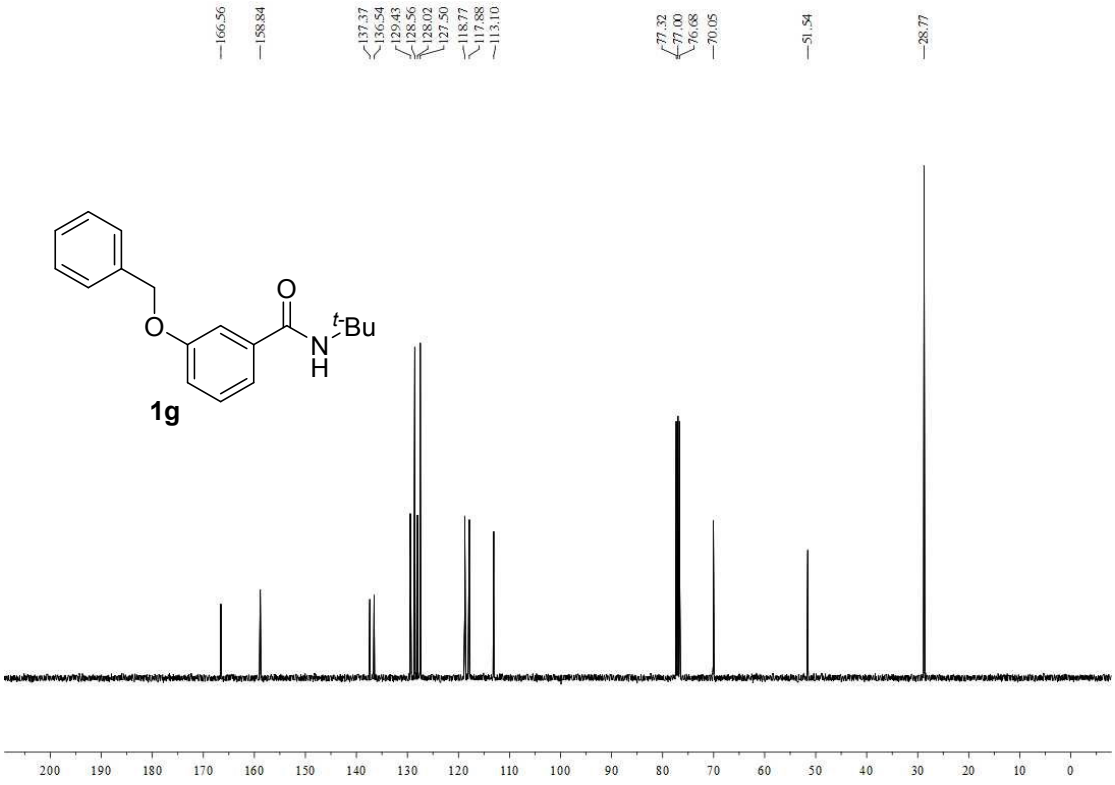
^{19}F NMR spectra in $CDCl_3$ for compound 1e



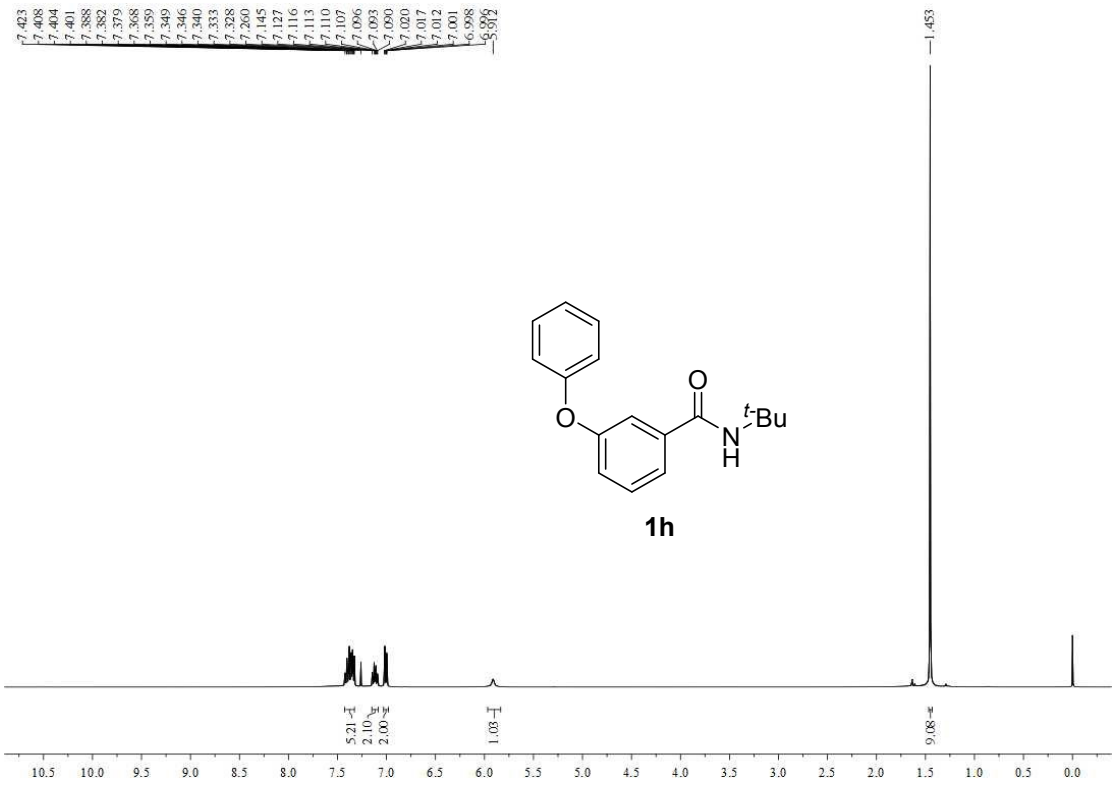


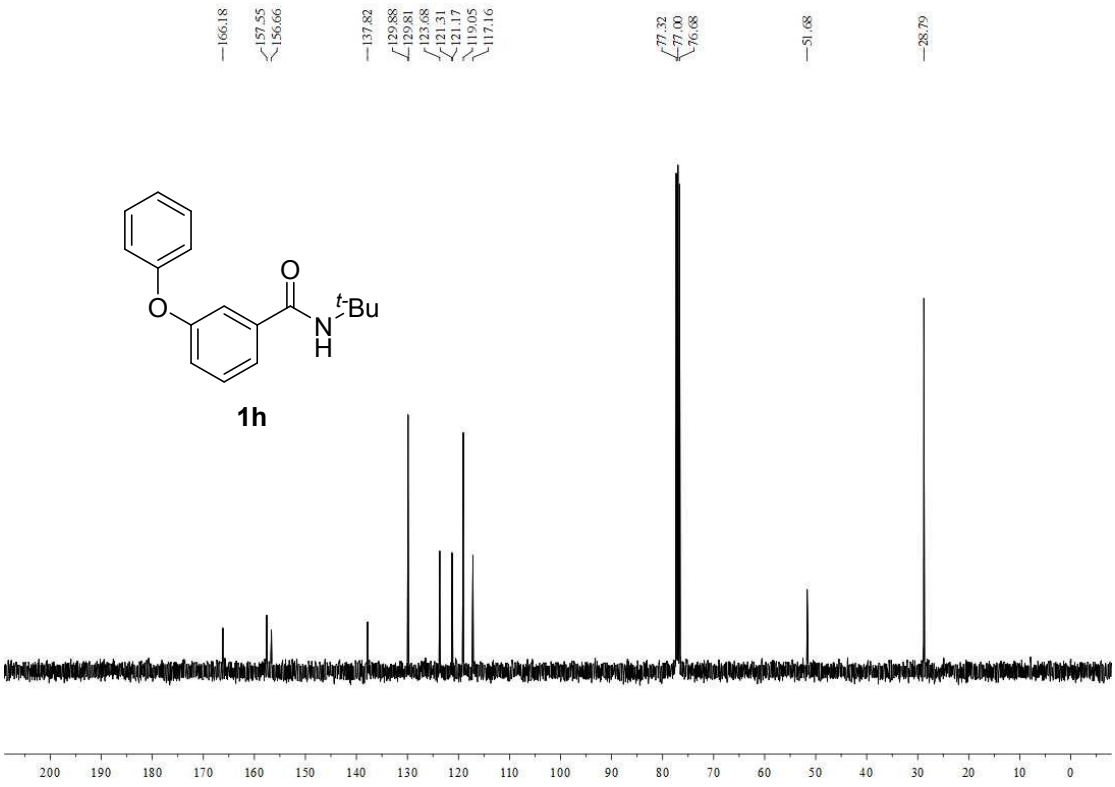
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1f



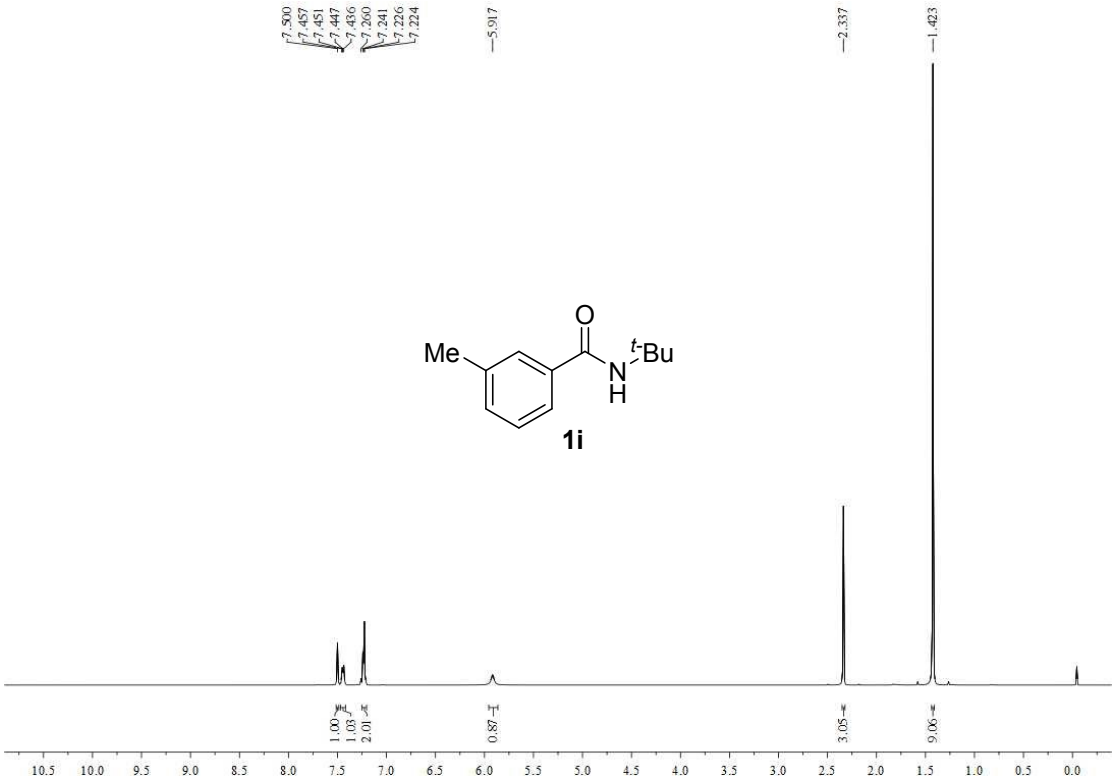


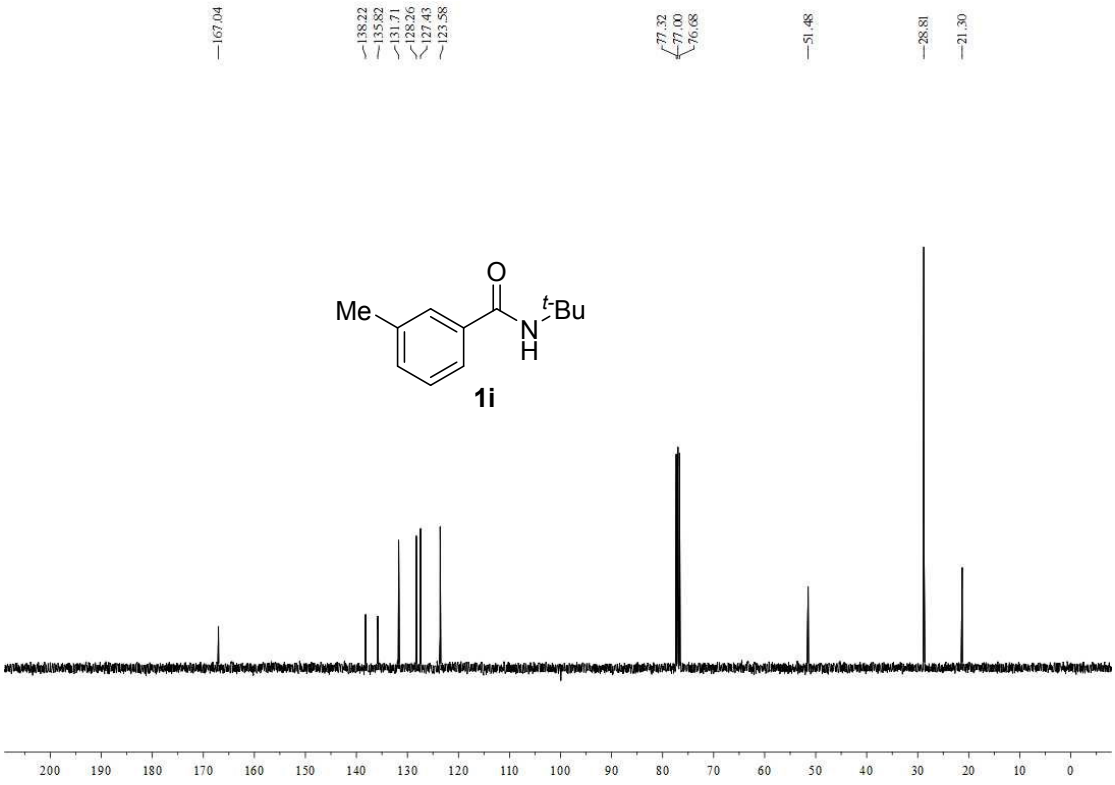
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1g



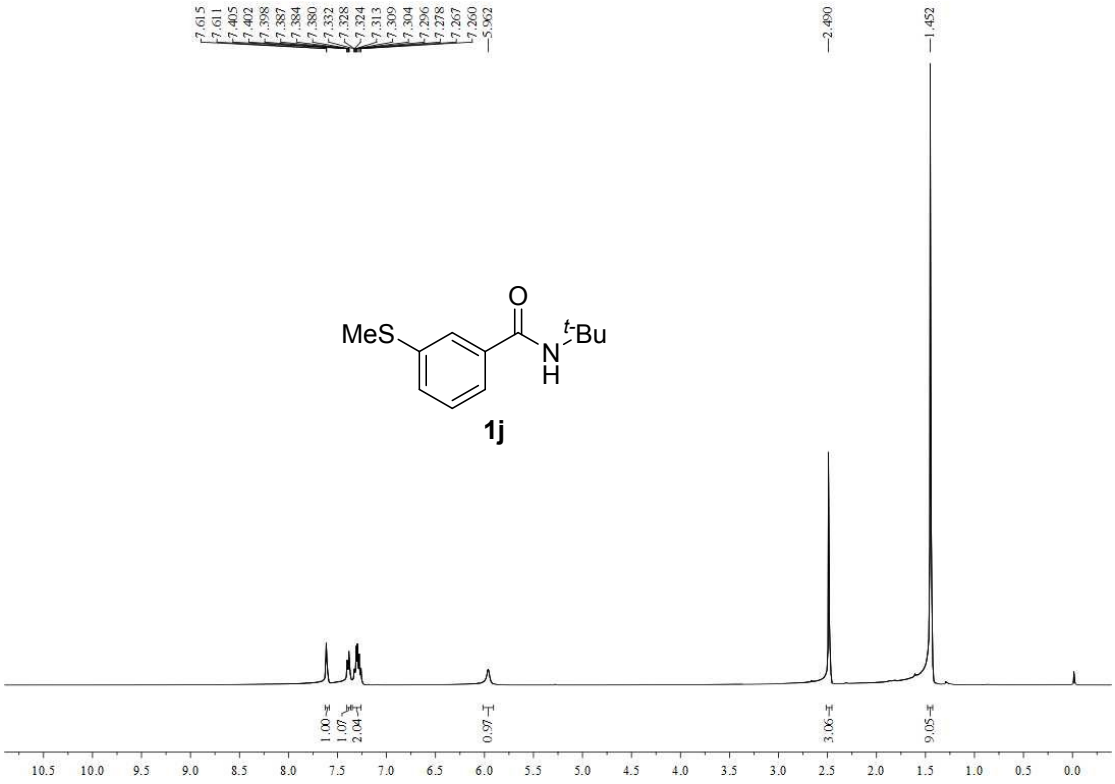


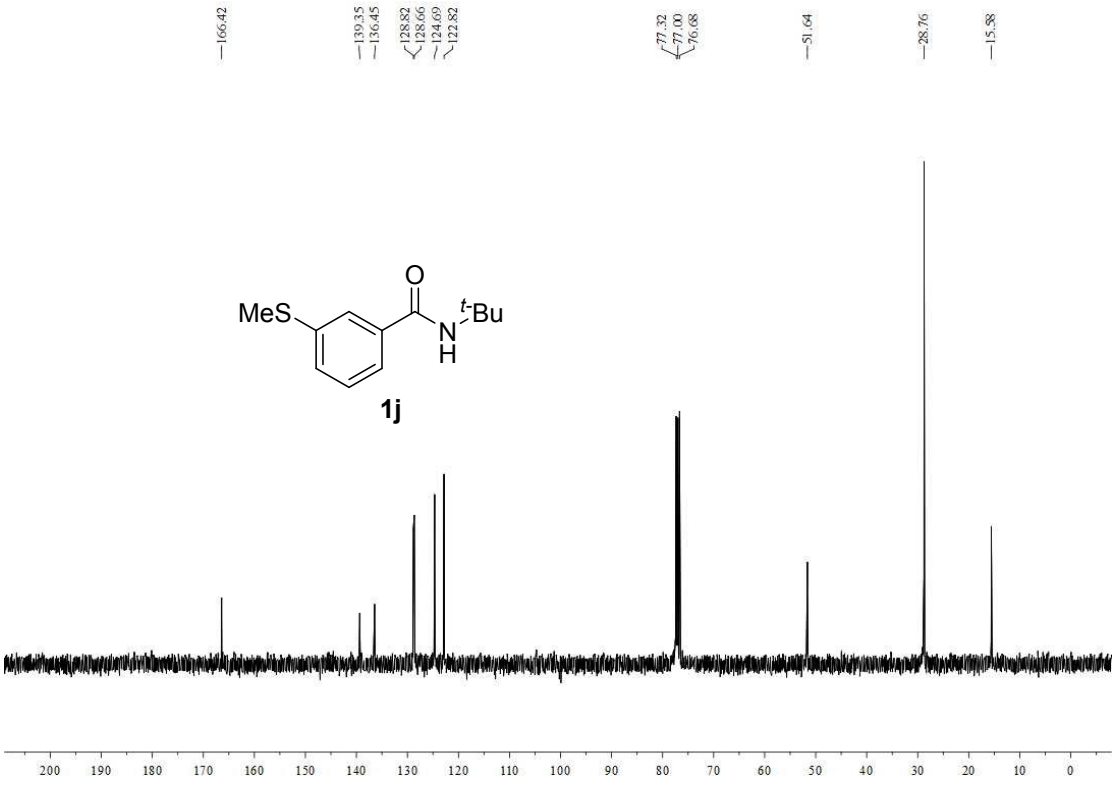
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1h



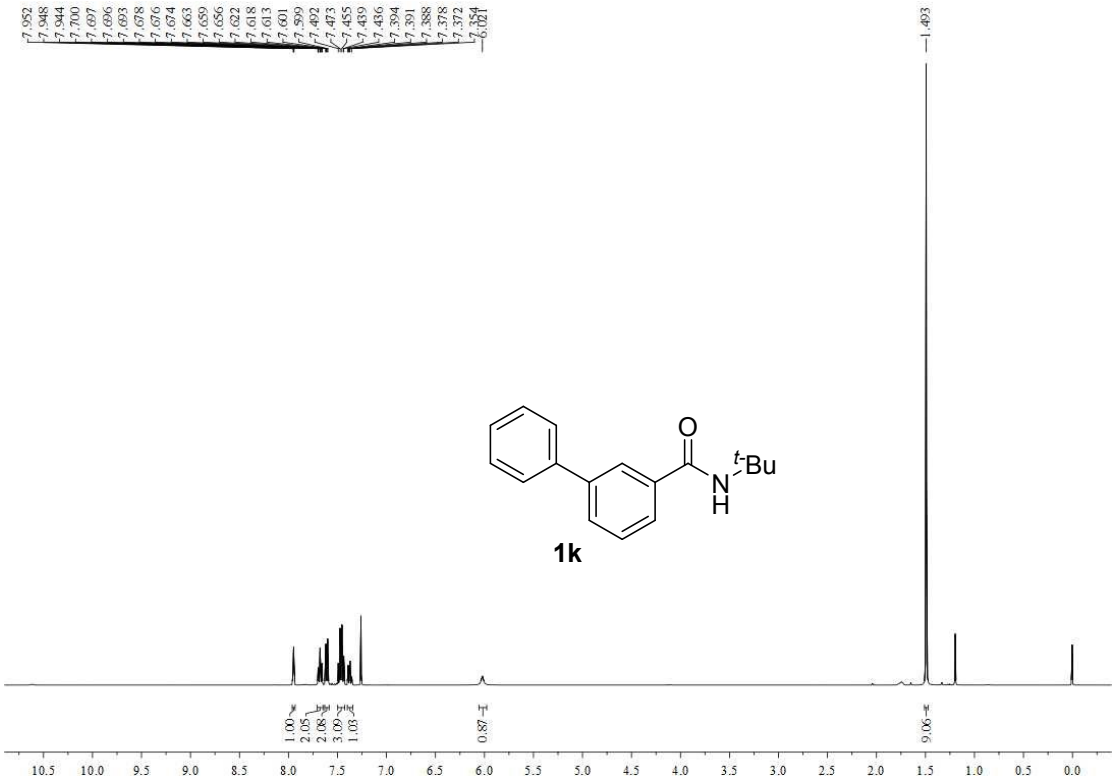


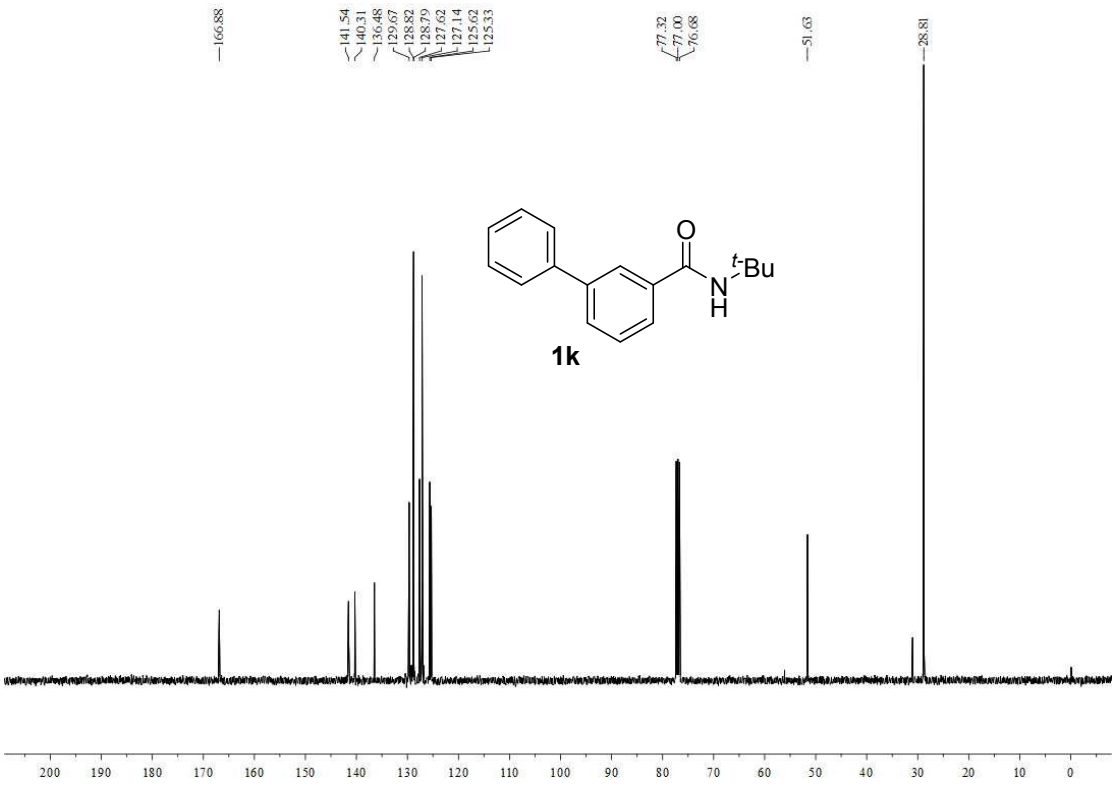
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1i



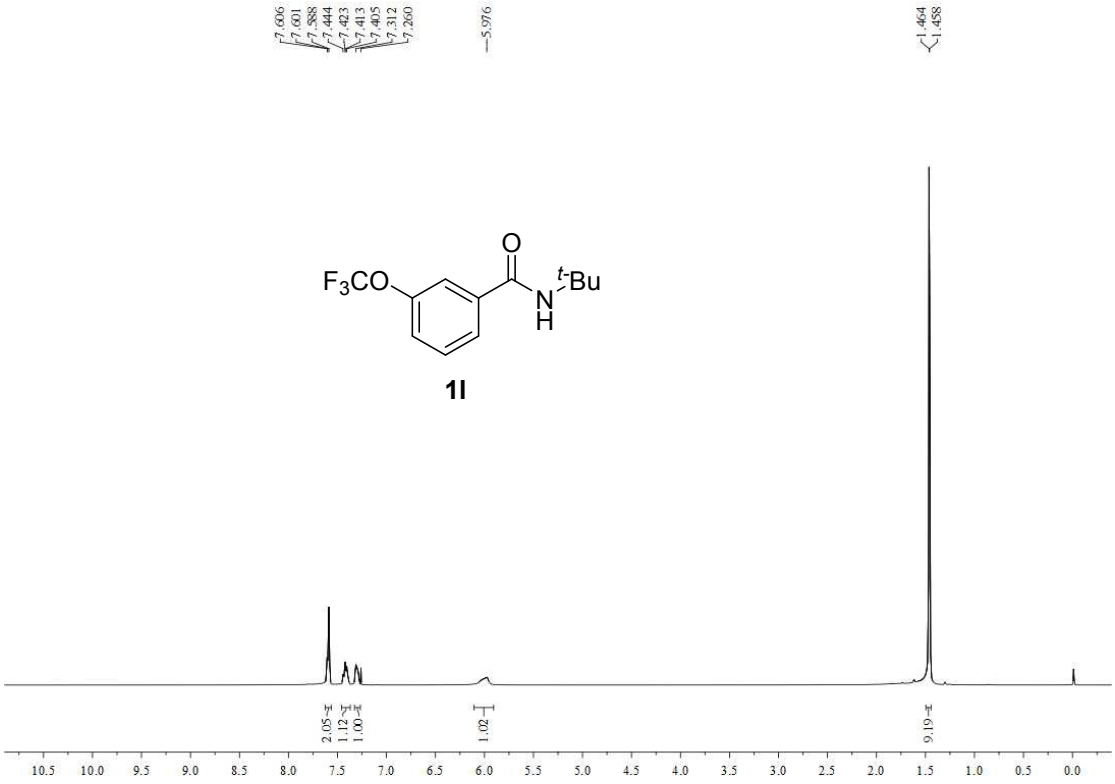


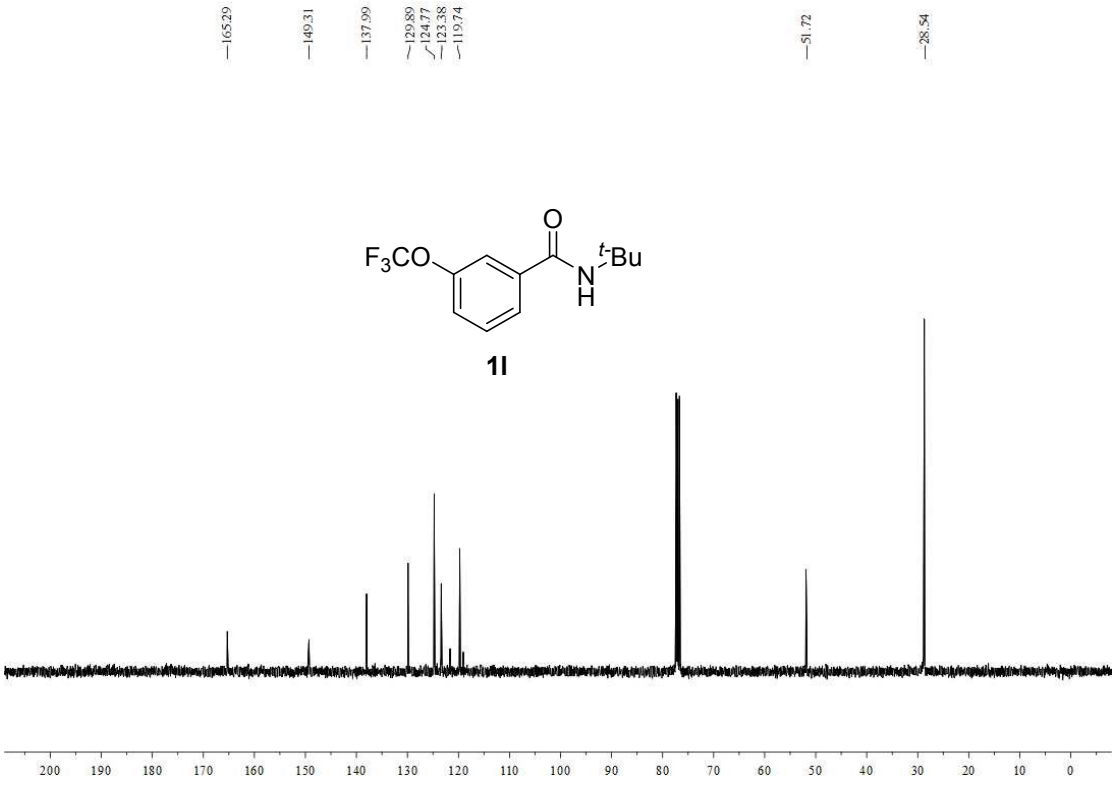
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1j



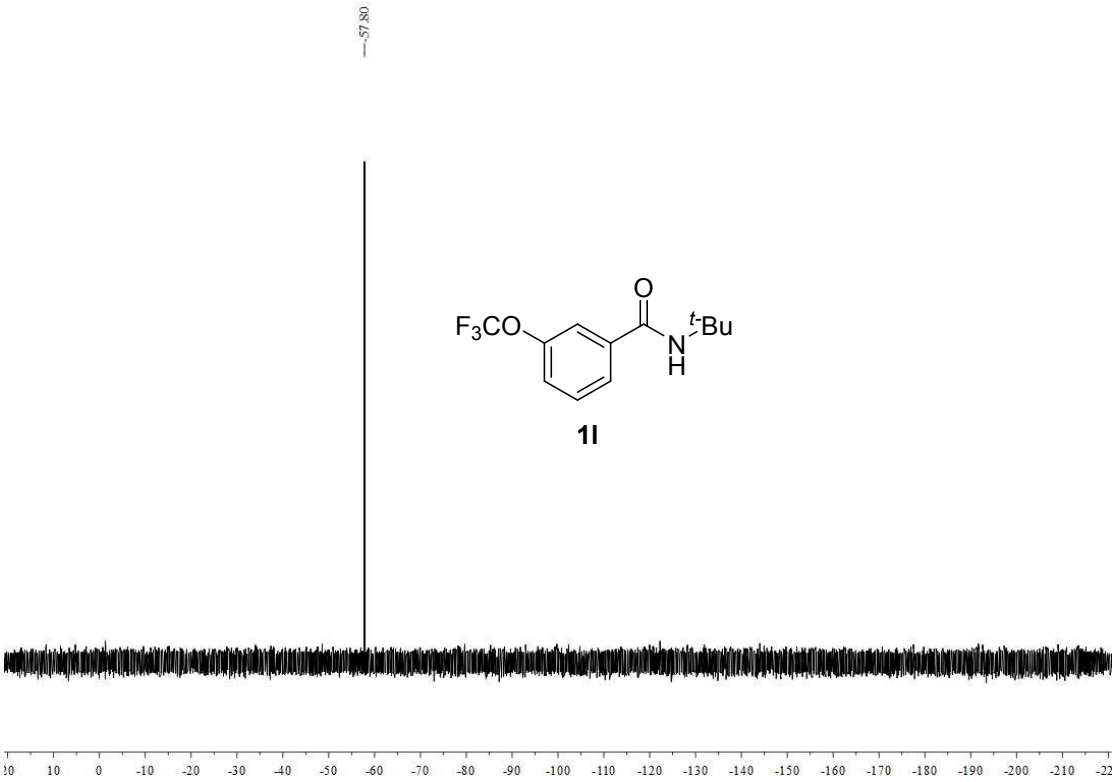


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1k

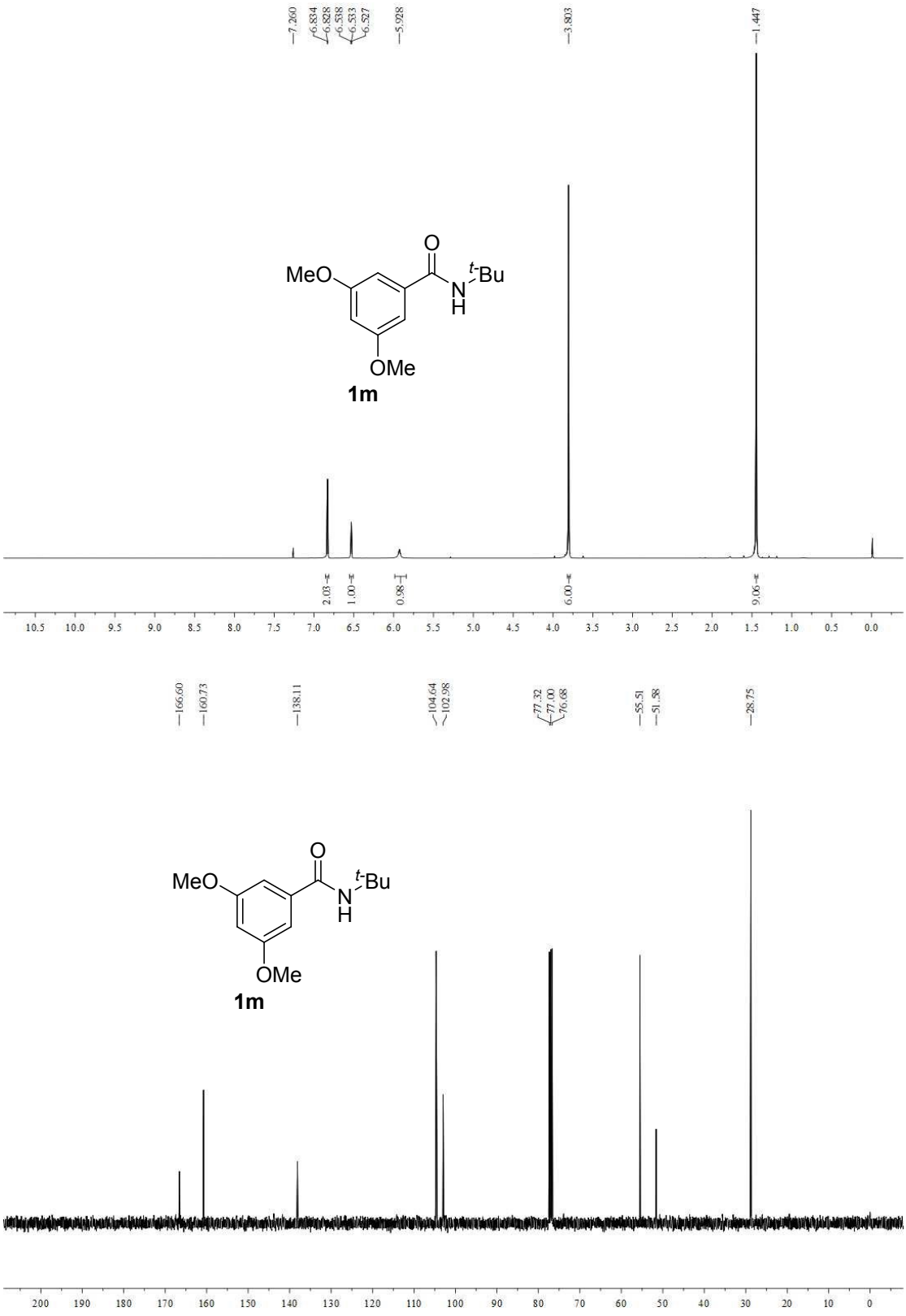




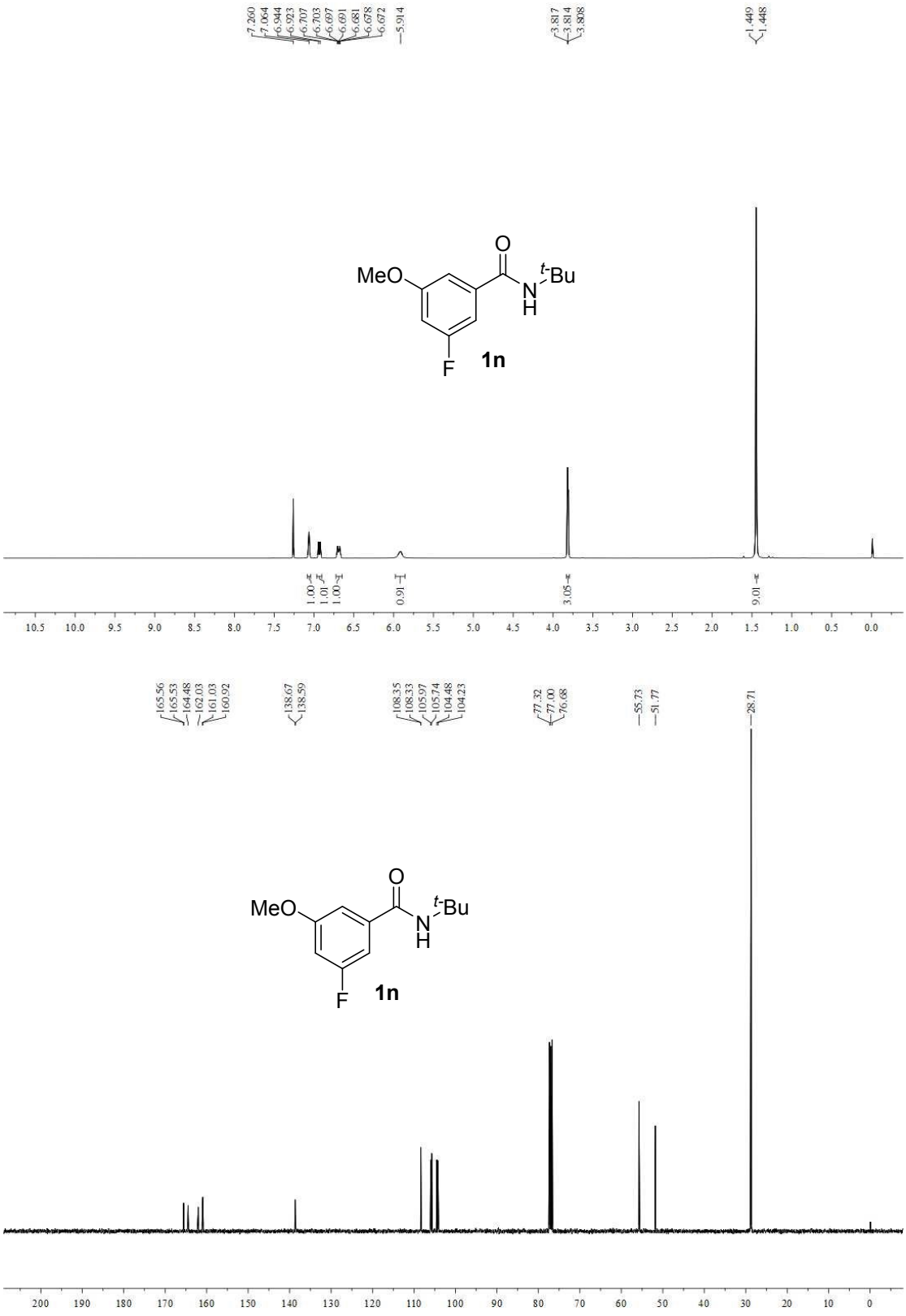
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1l



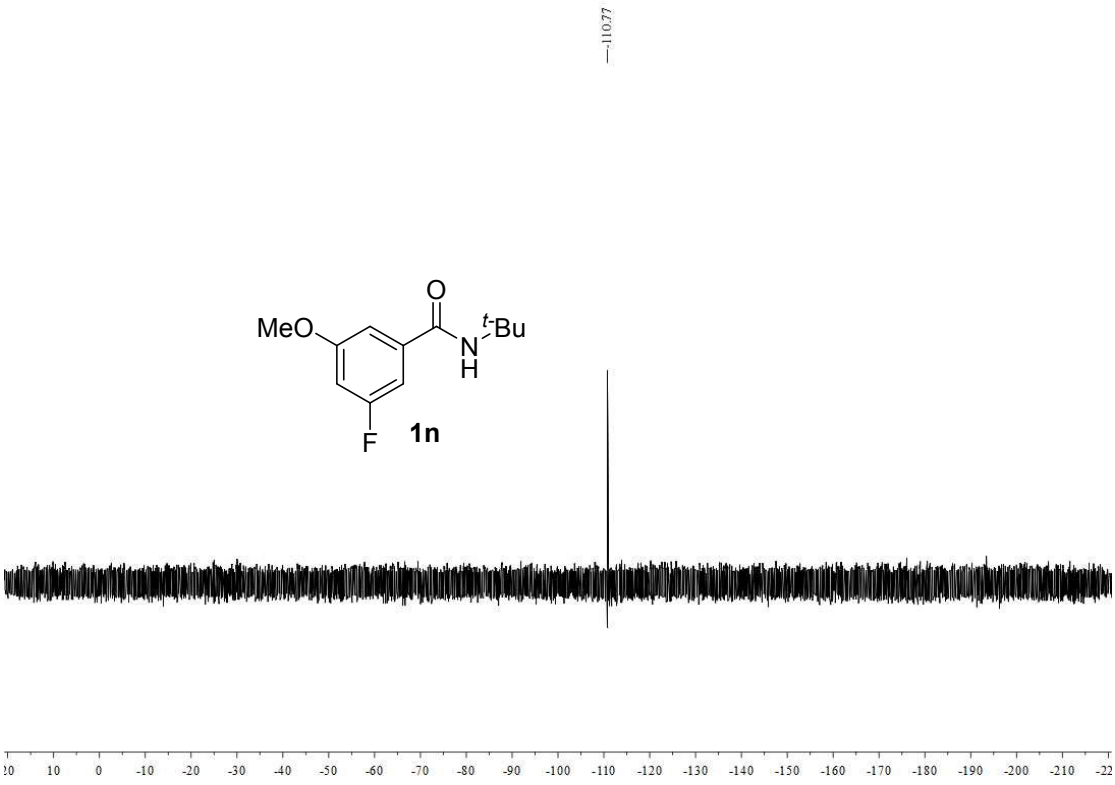
^{19}F NMR spectra in $CDCl_3$ for compound 1l



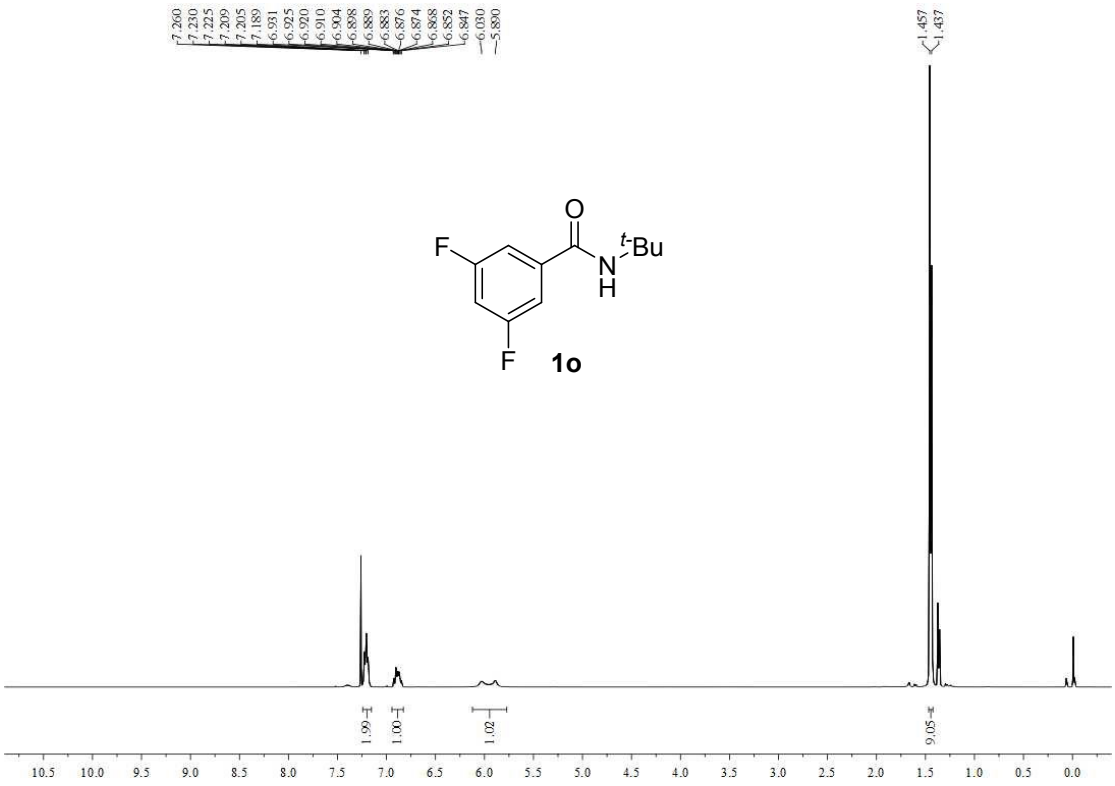
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1m

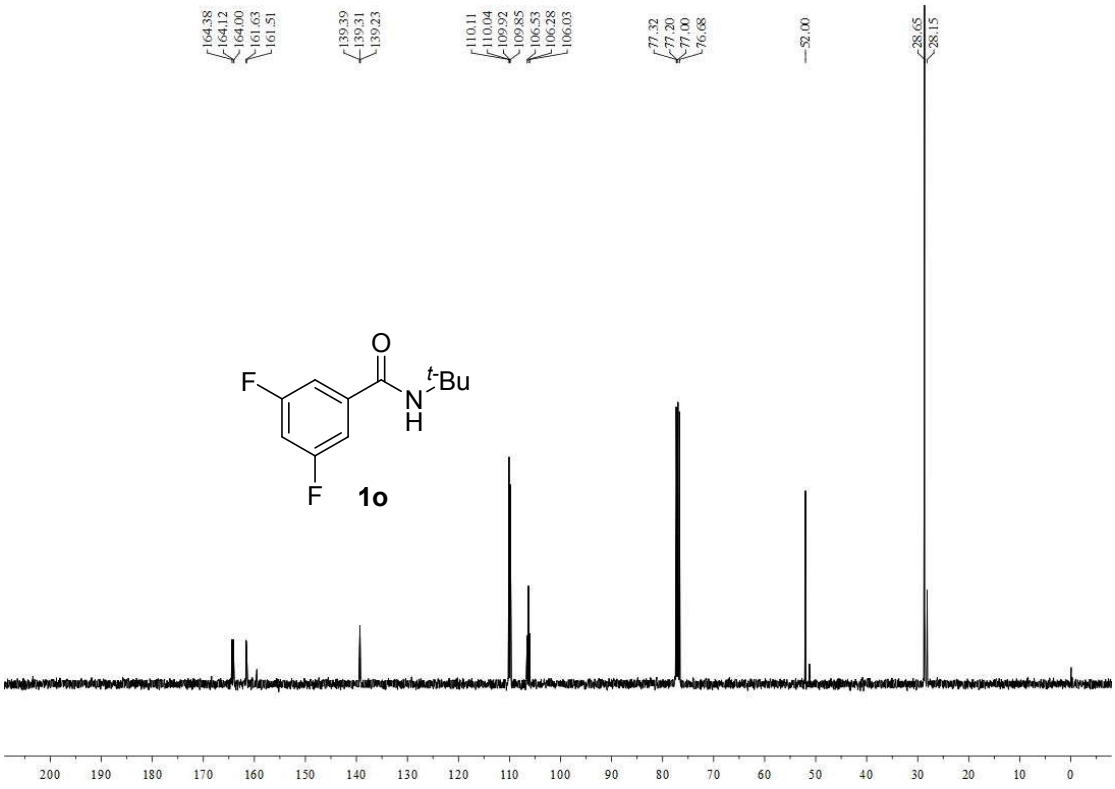


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1n

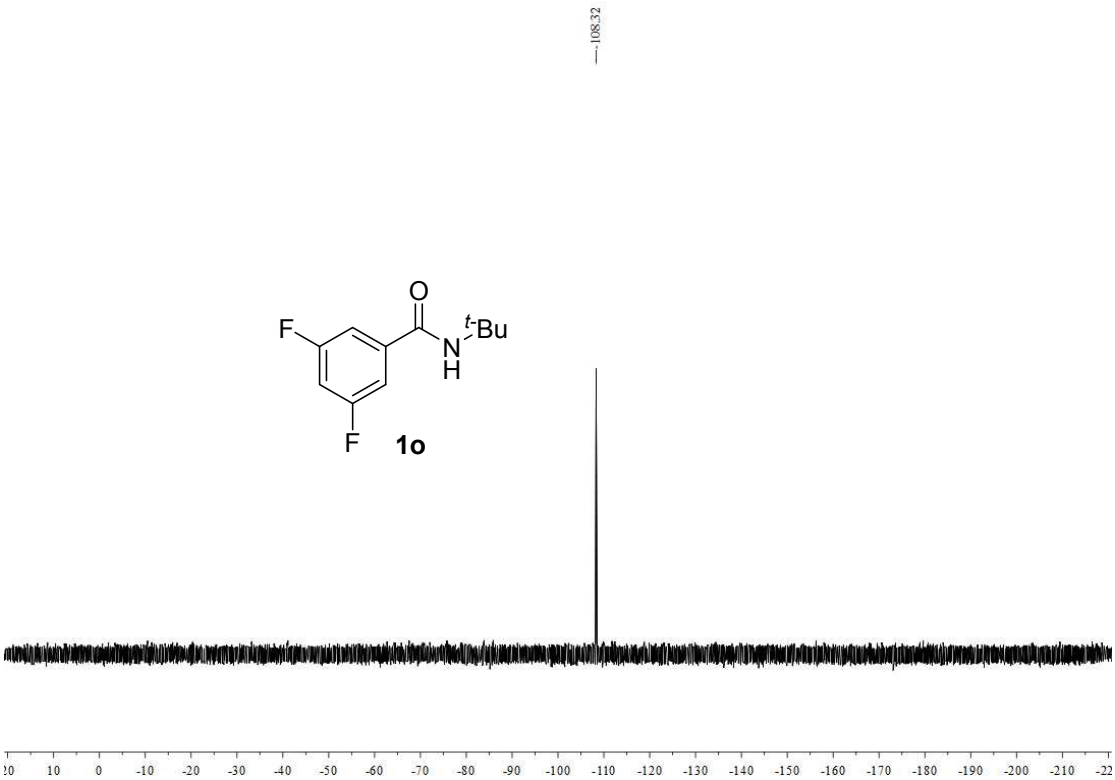


^{19}F NMR spectra in $CDCl_3$ for compound 1n

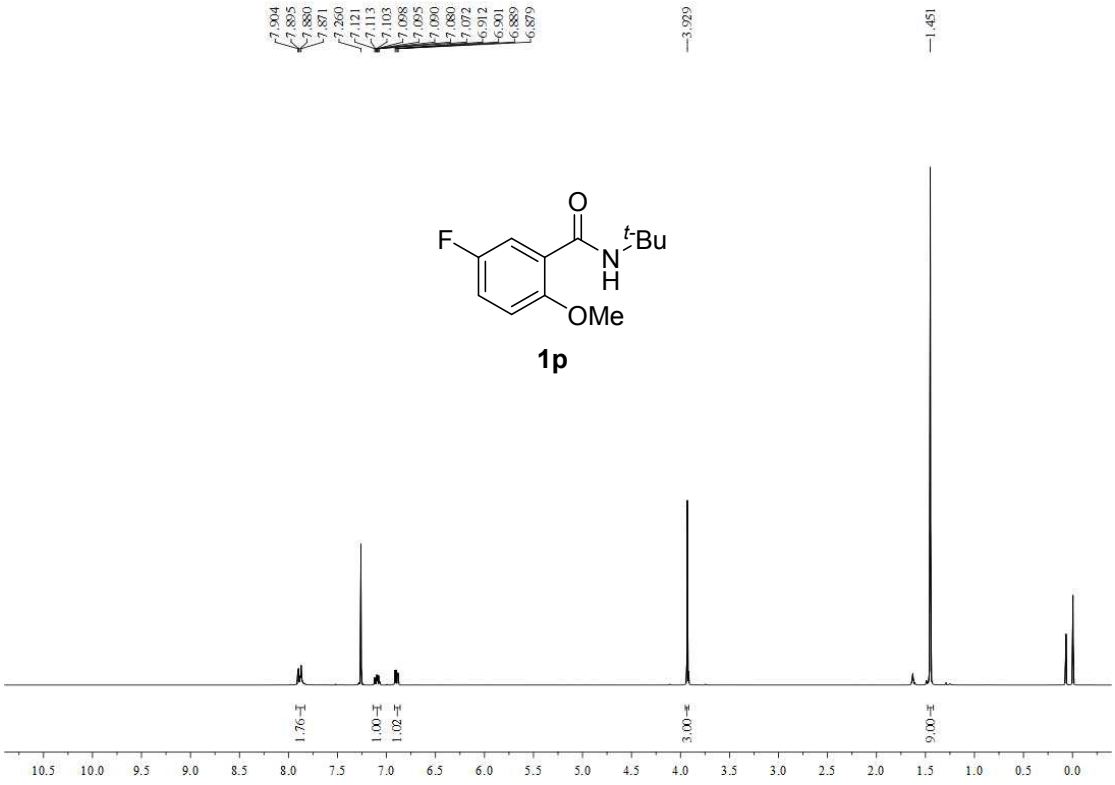


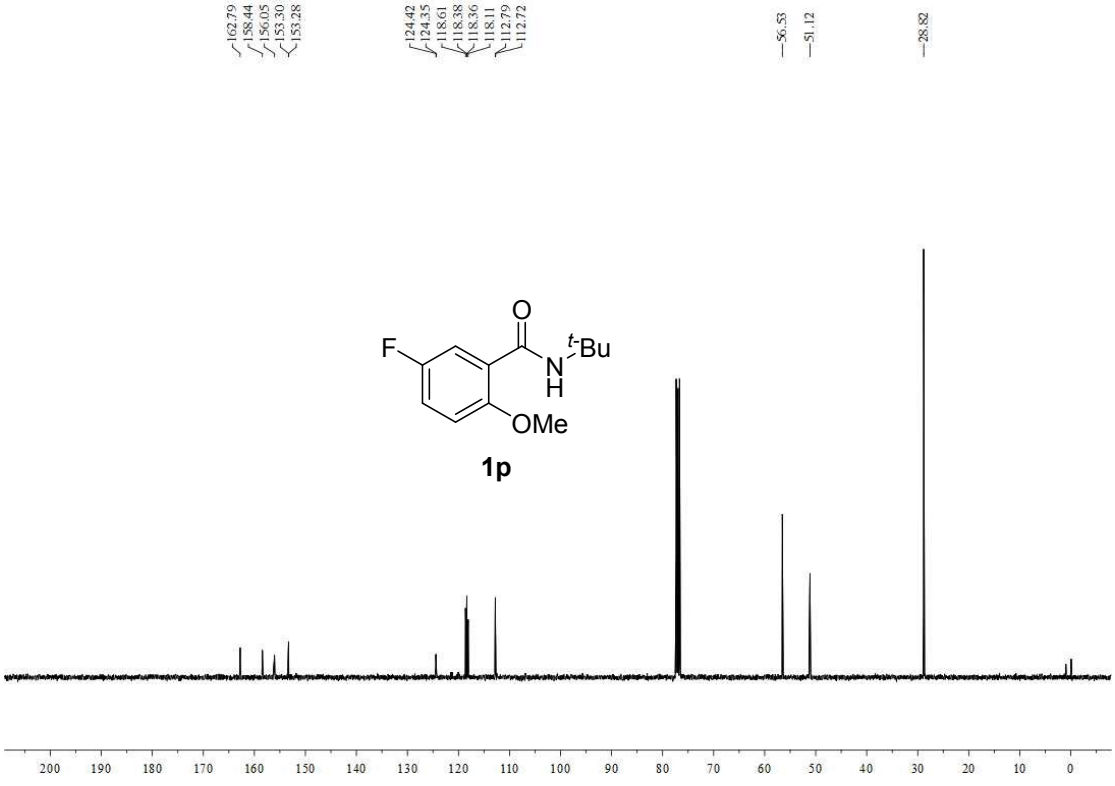


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1o

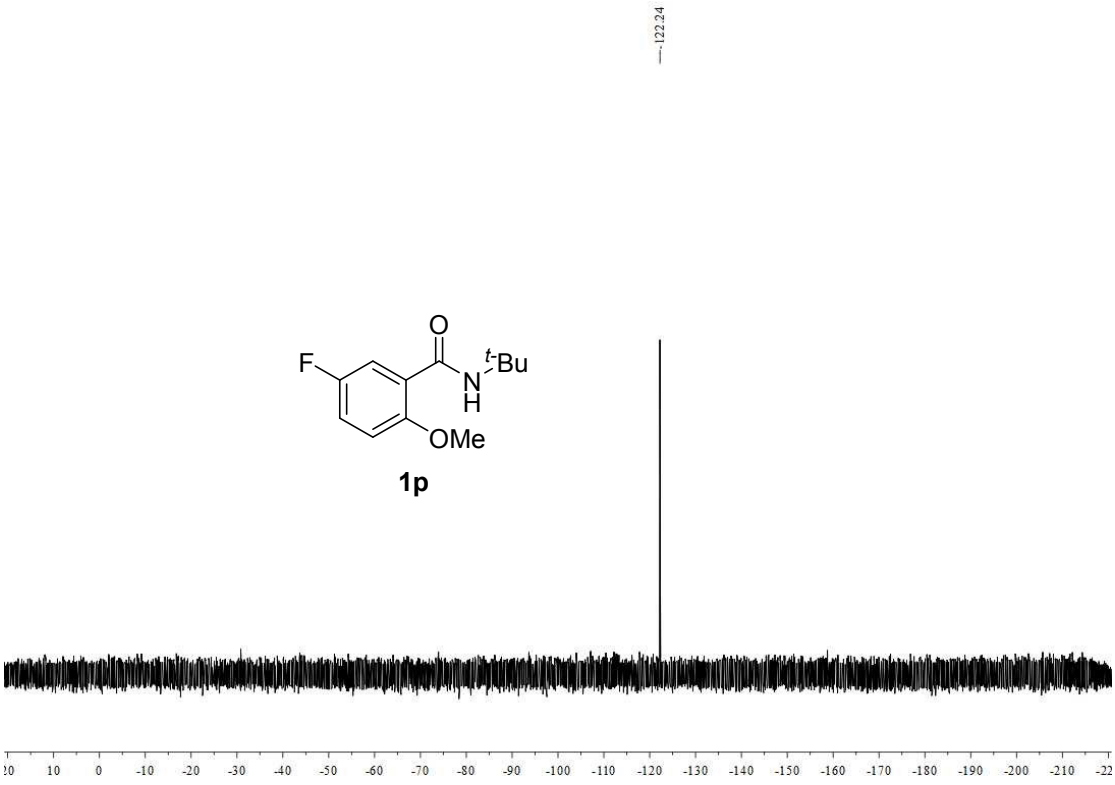


^{19}F NMR spectra in $CDCl_3$ for compound 1p

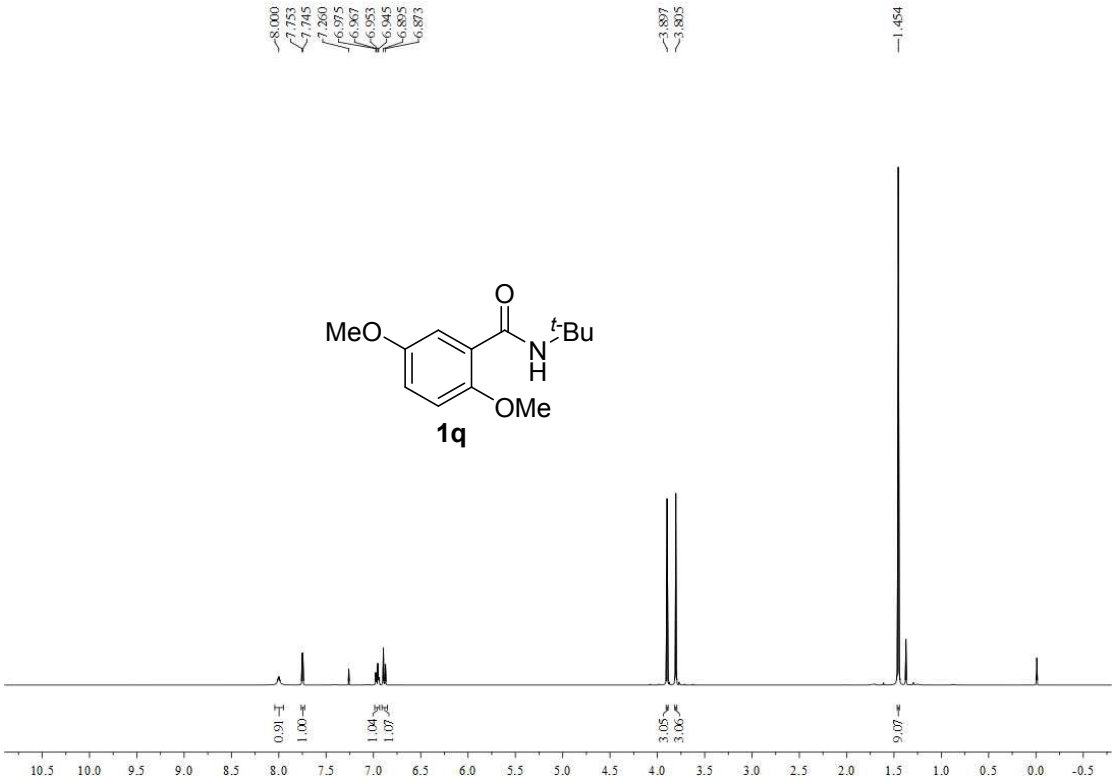


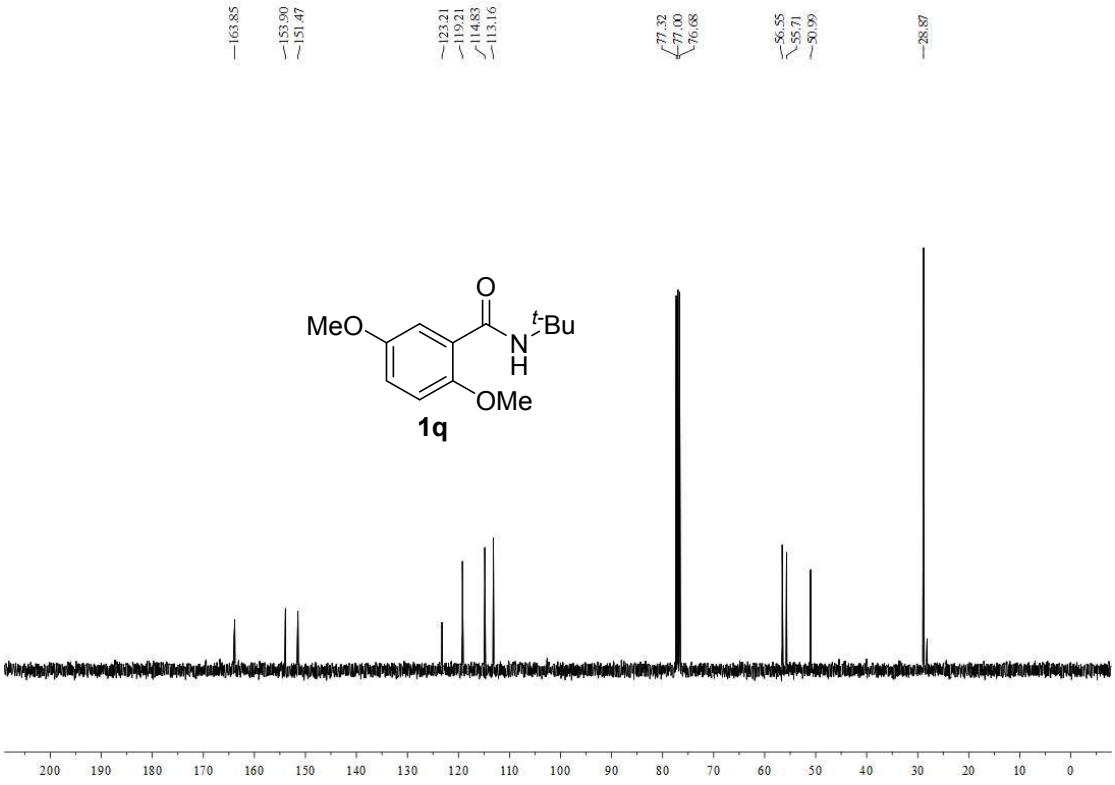


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1p

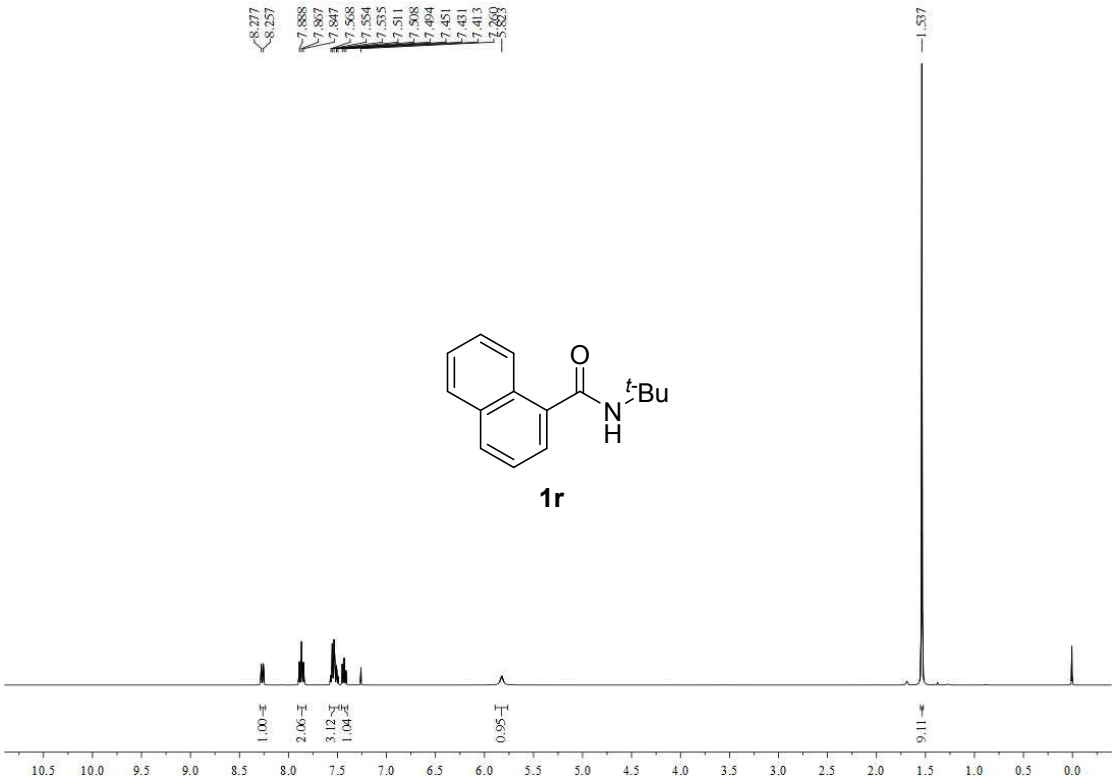


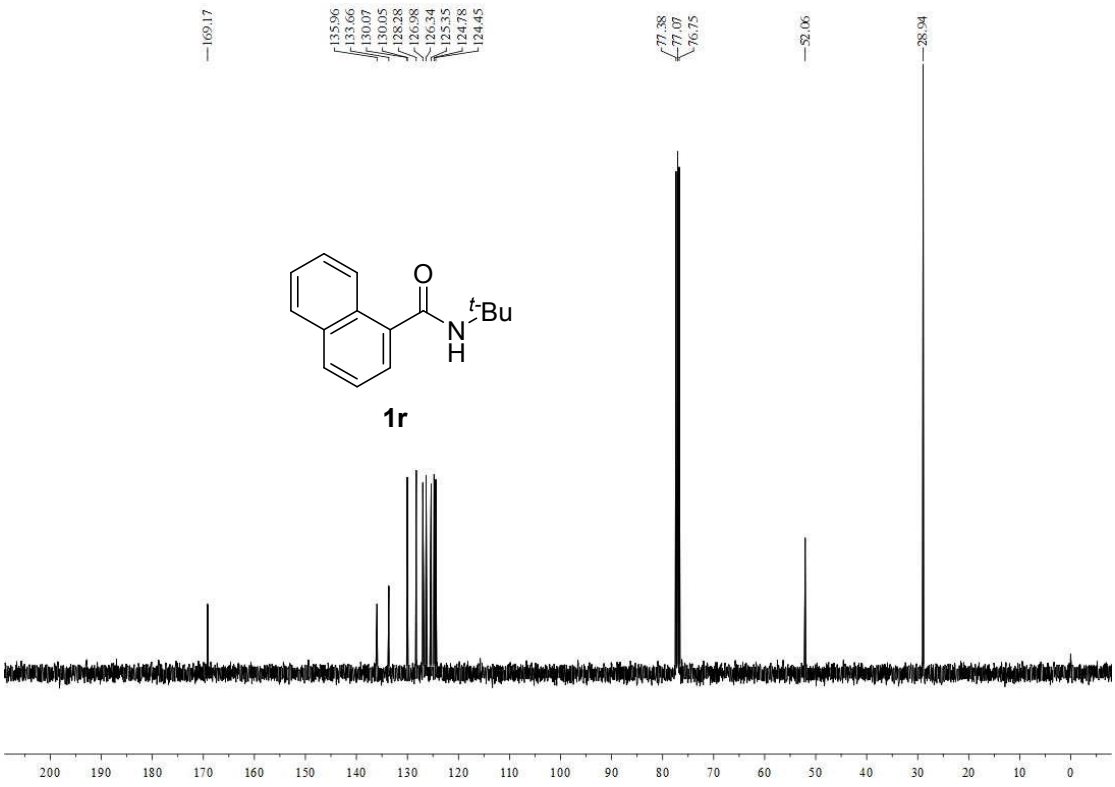
^{19}F NMR spectra in $CDCl_3$ for compound 1p



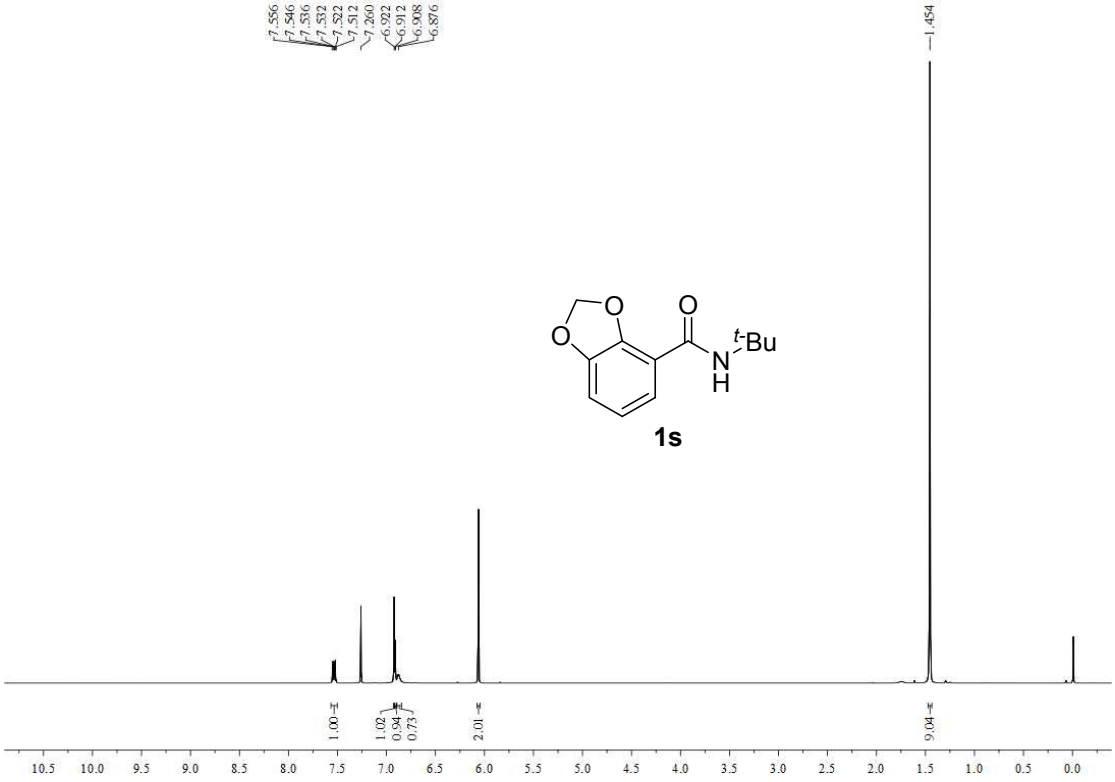


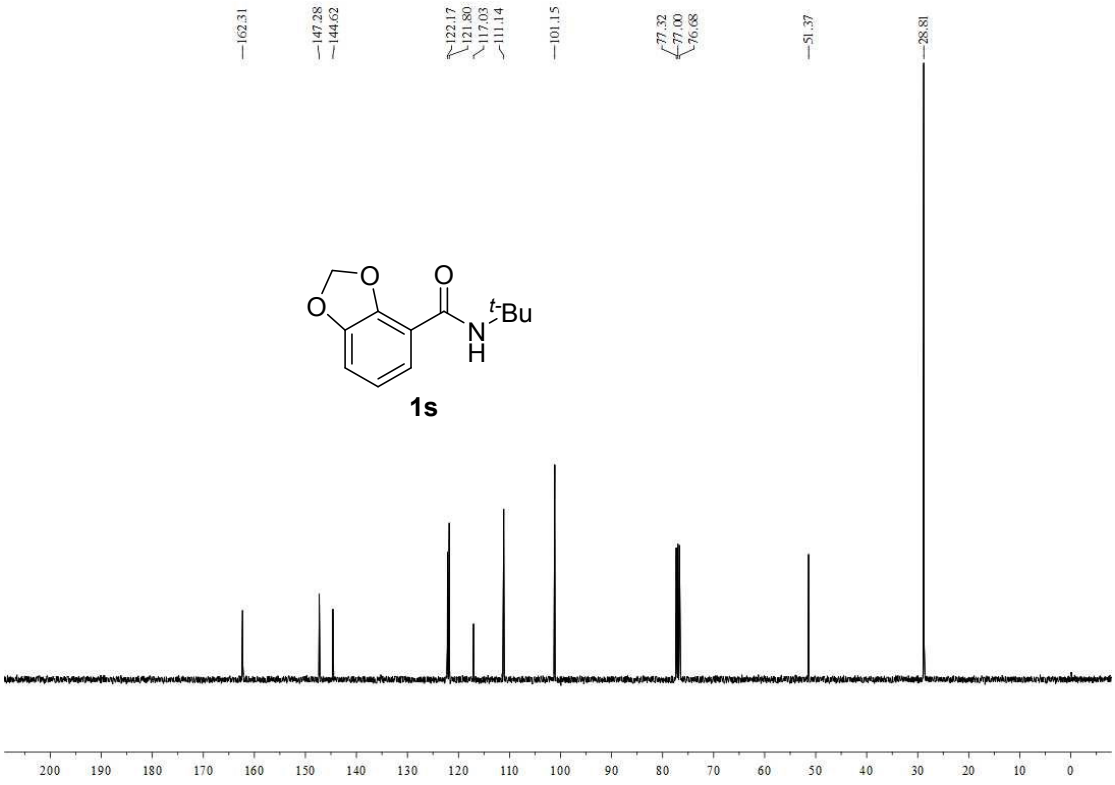
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1q



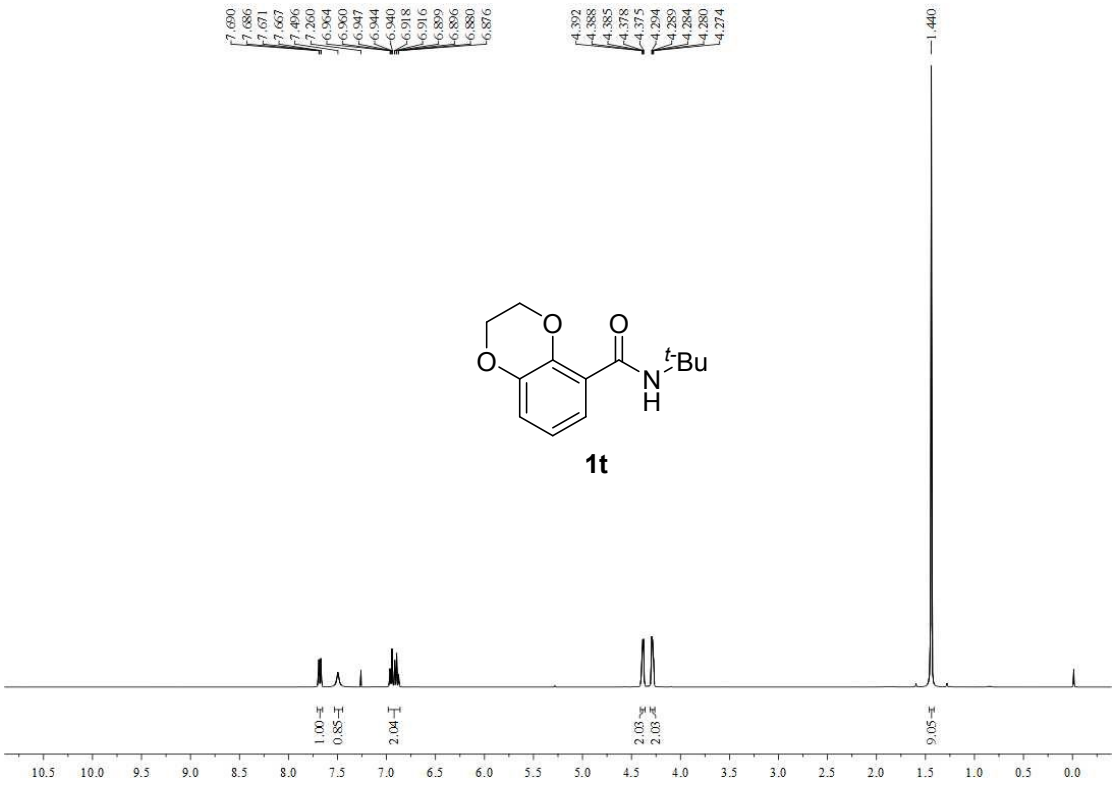


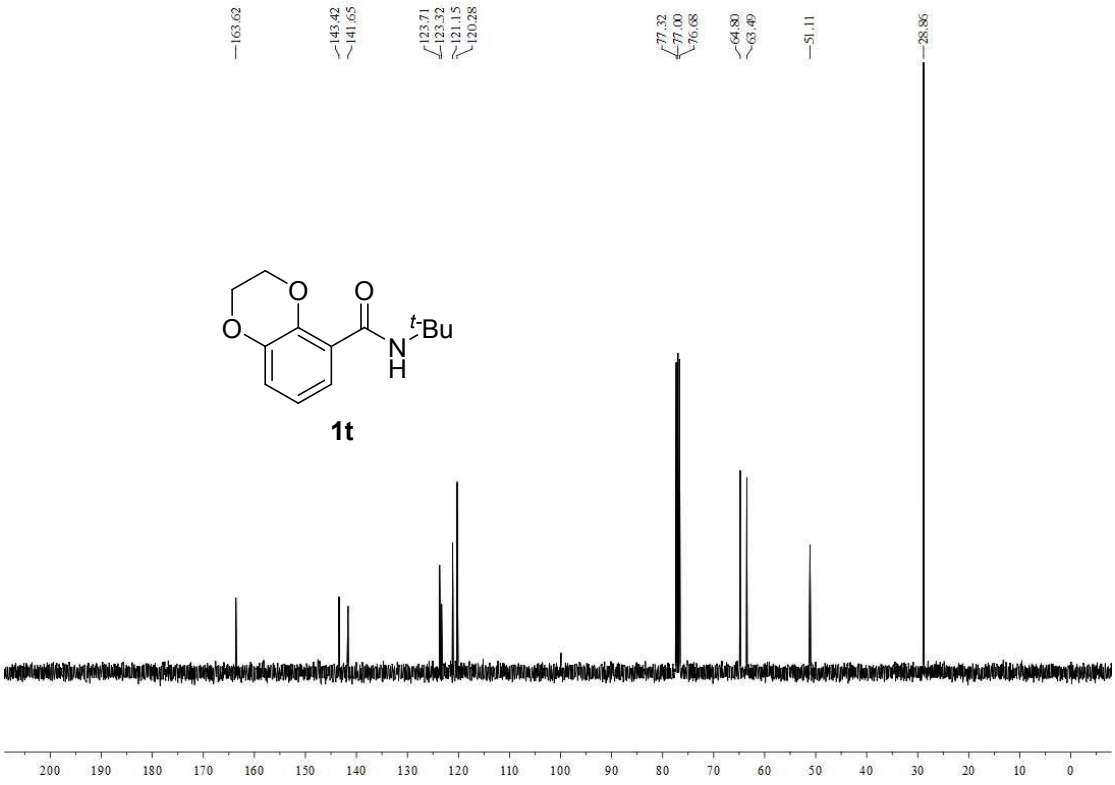
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1r



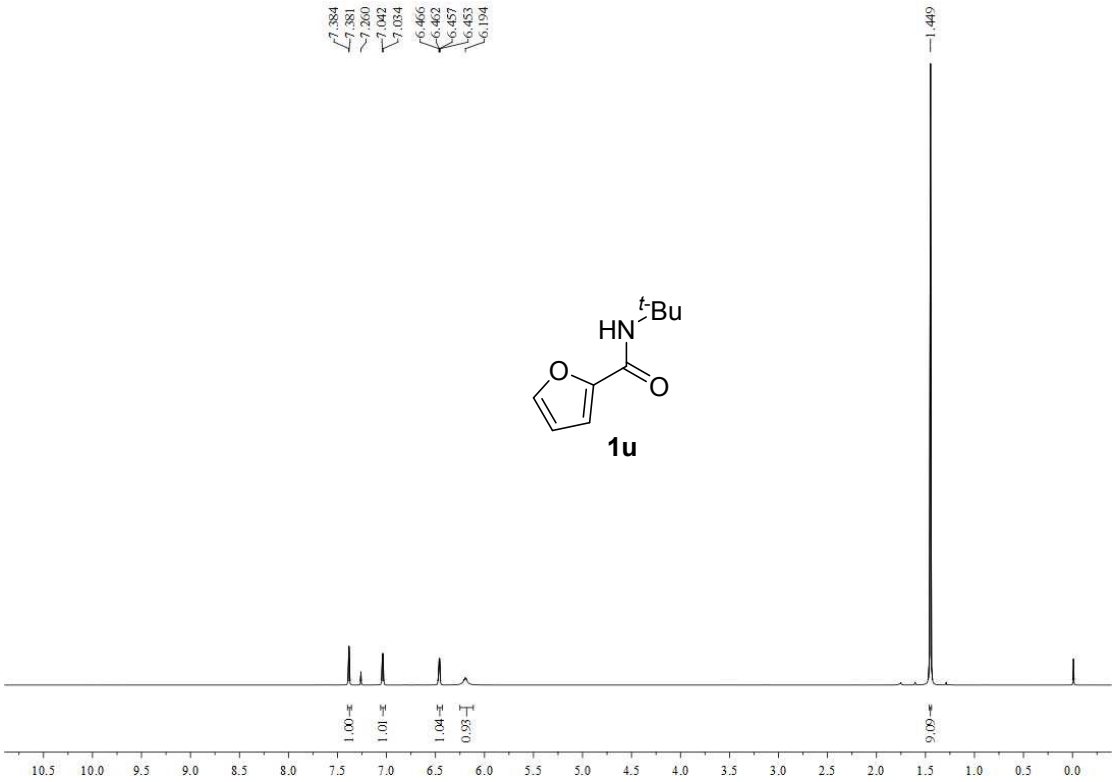


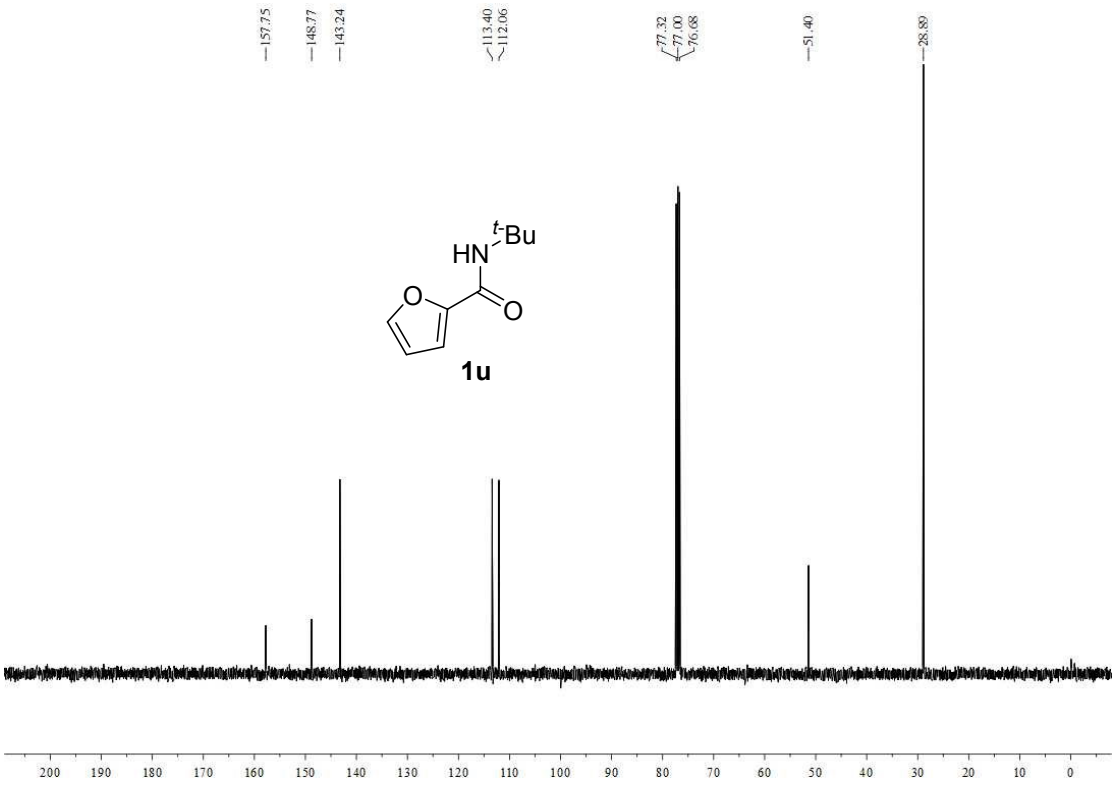
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1s



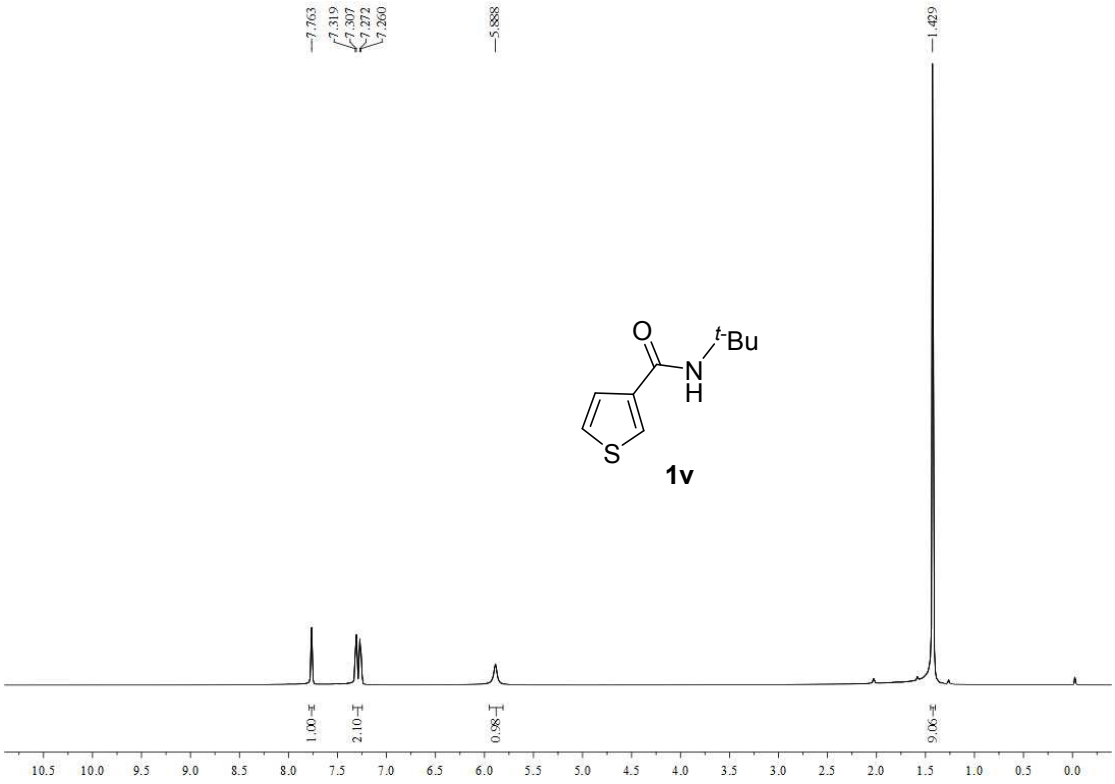


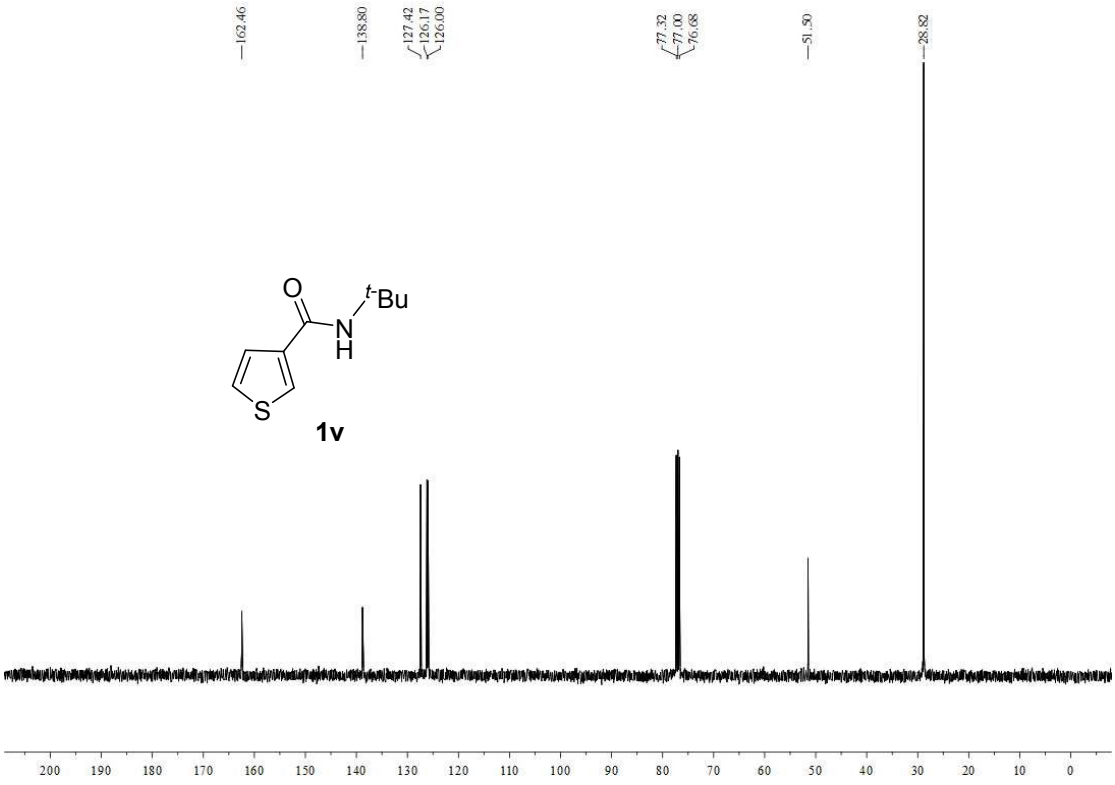
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1t



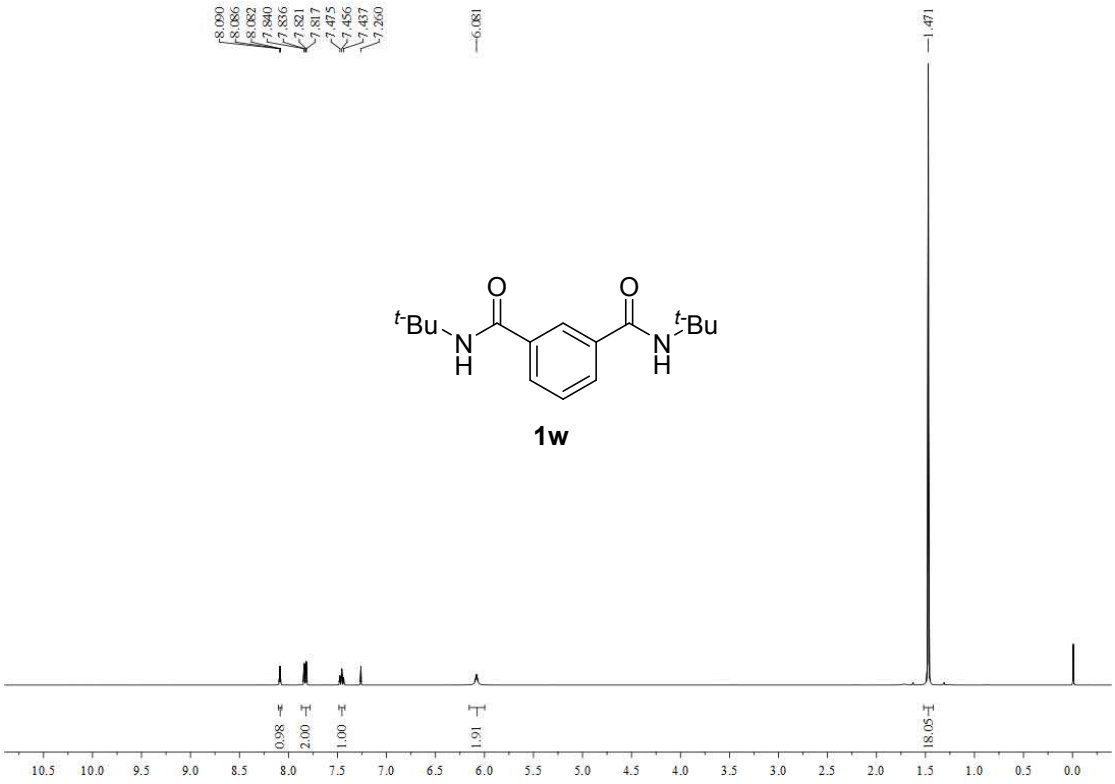


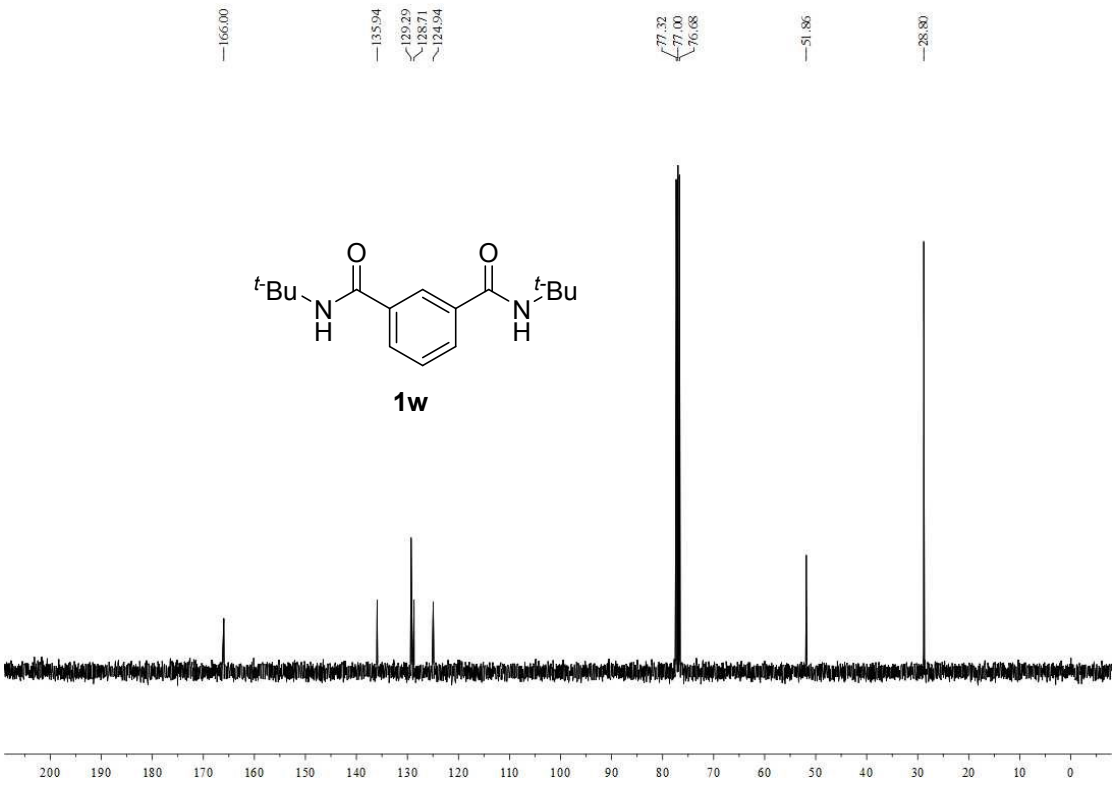
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1u



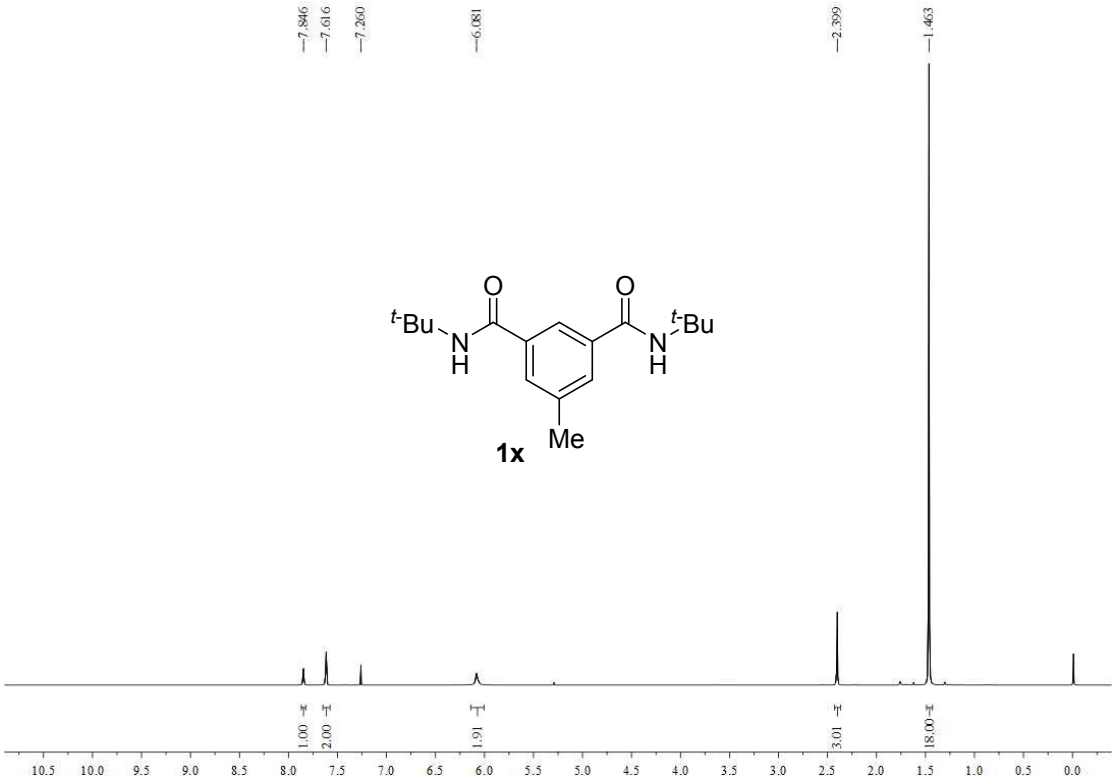


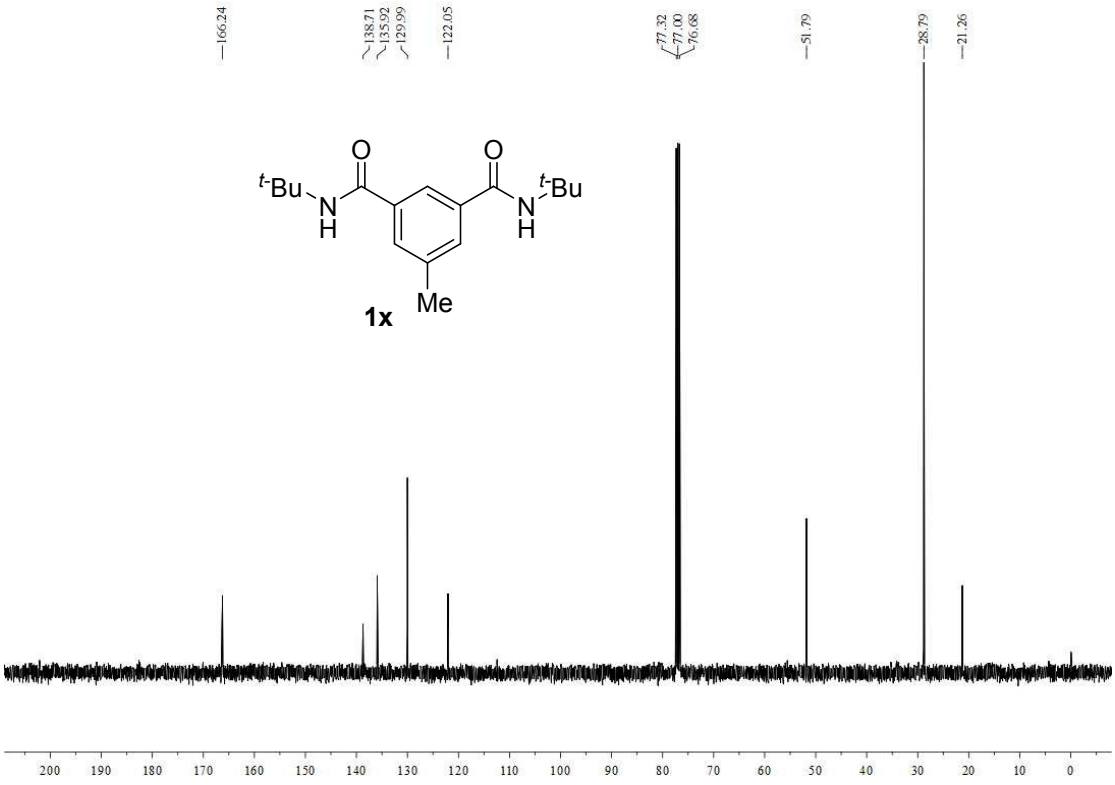
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1v



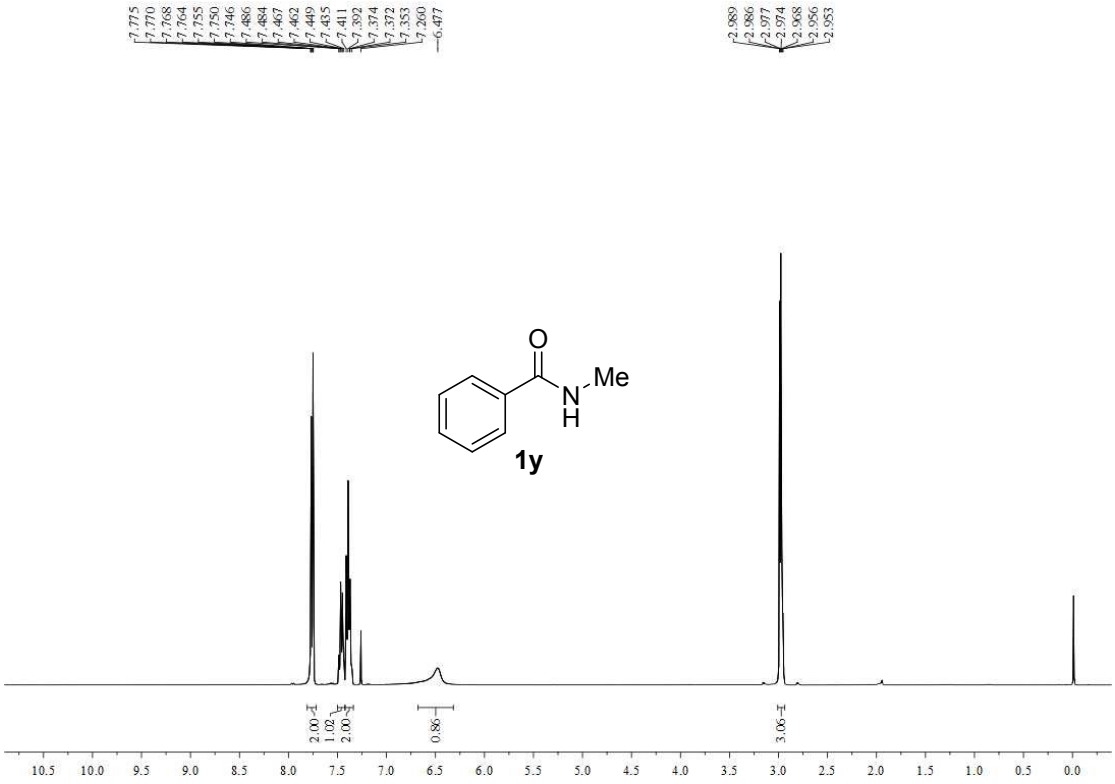


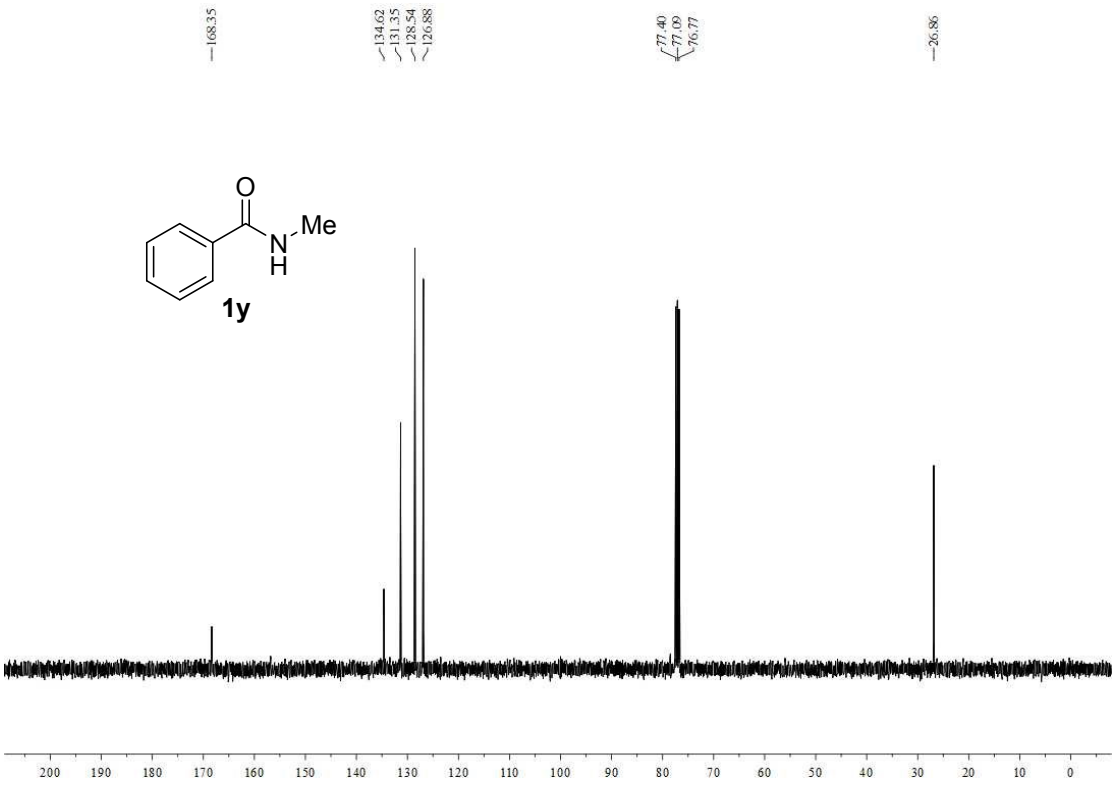
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1w



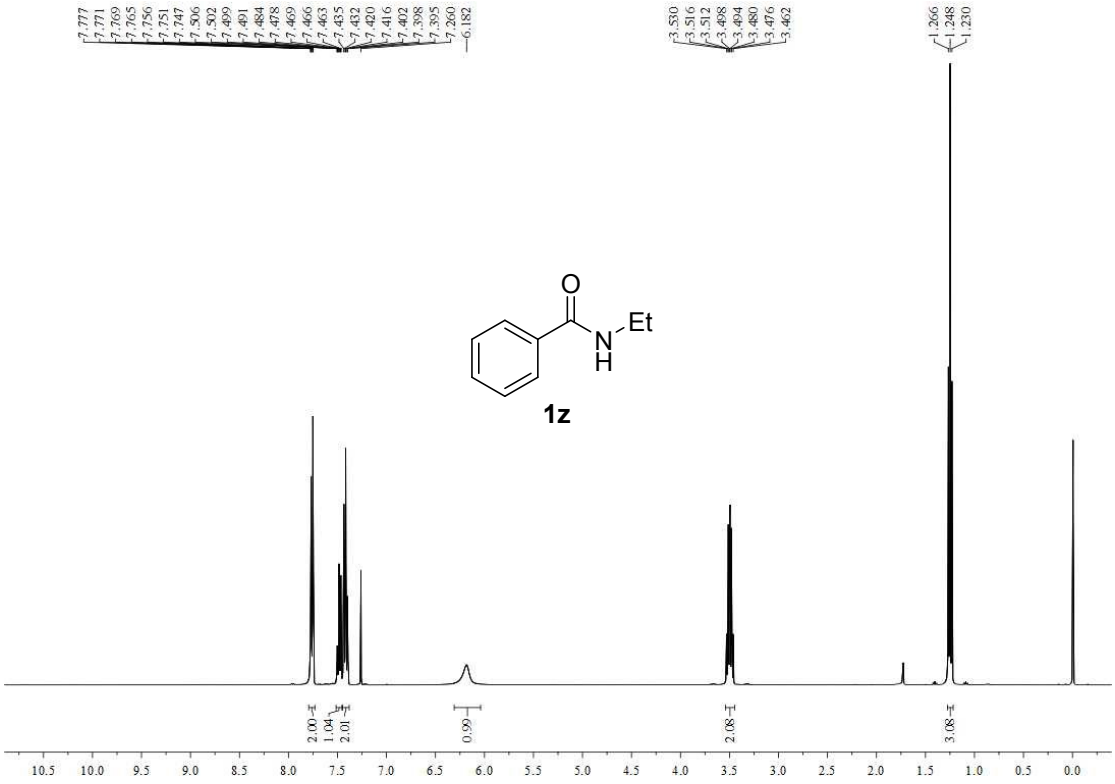


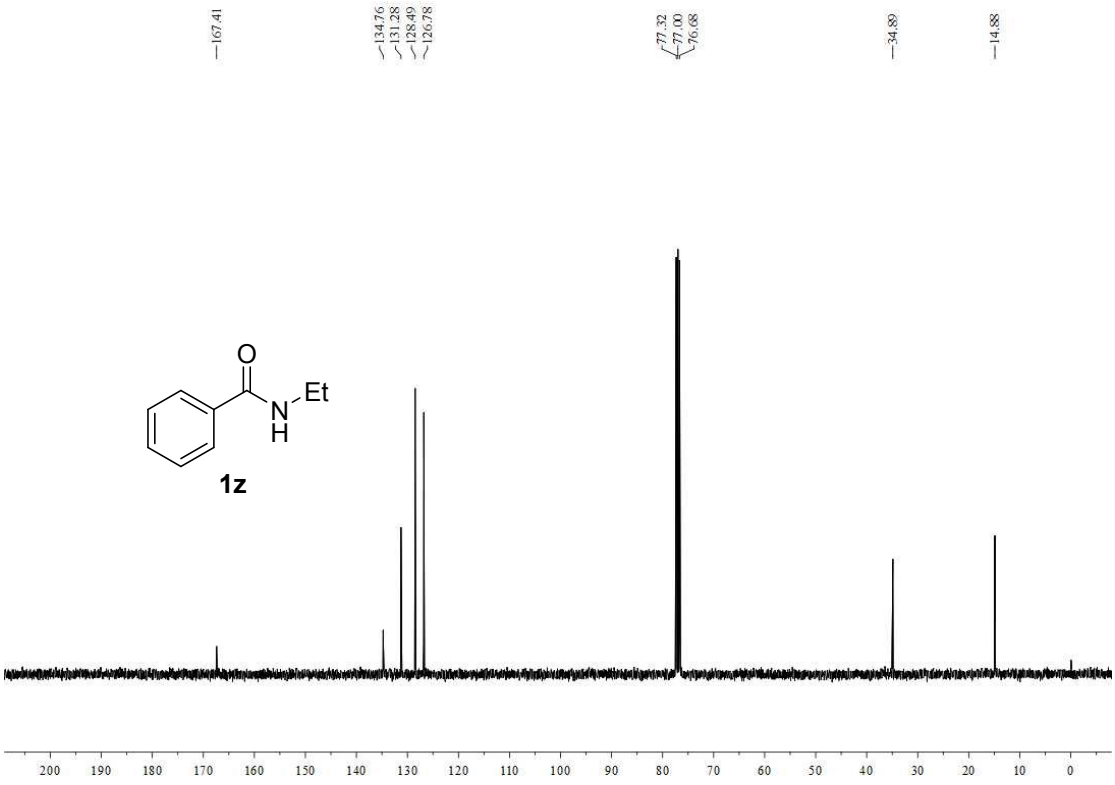
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1x



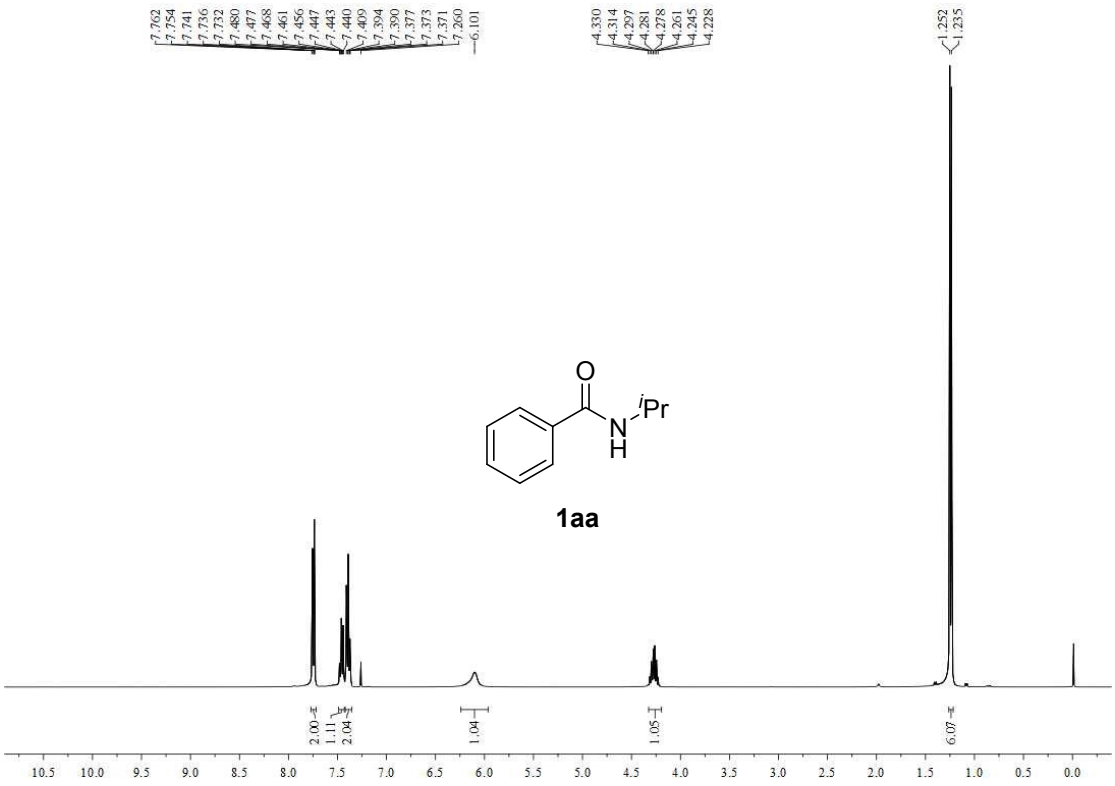


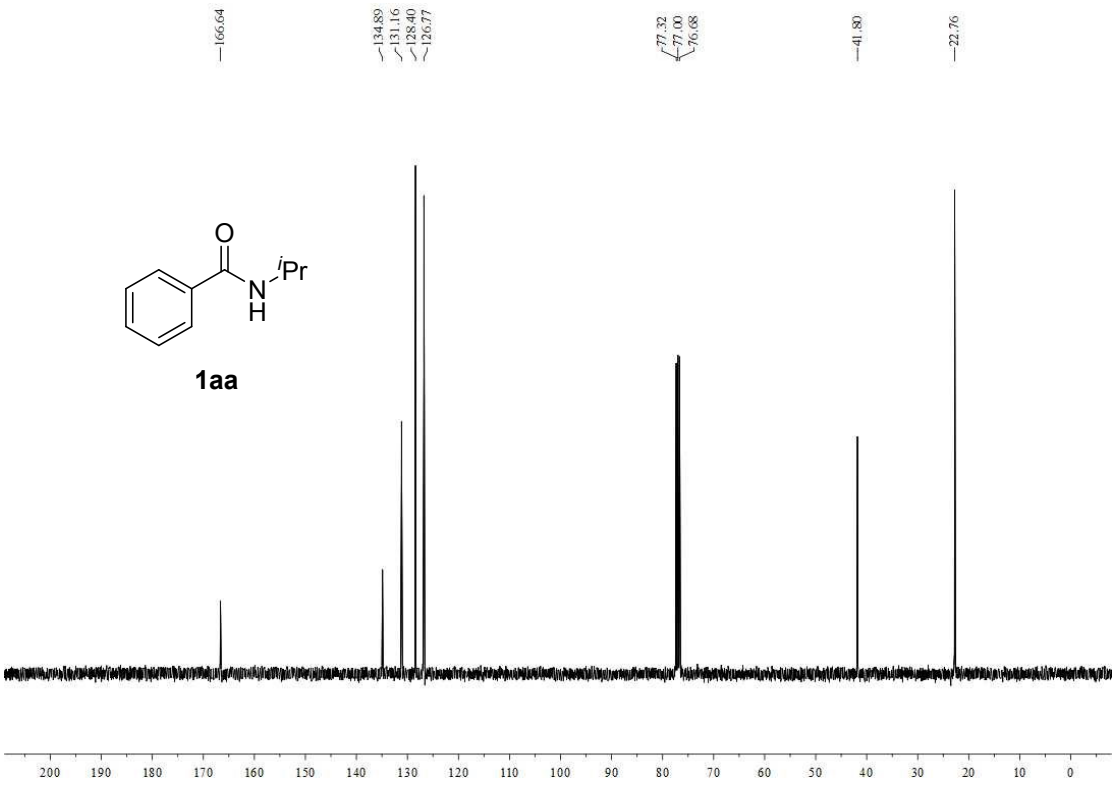
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1y



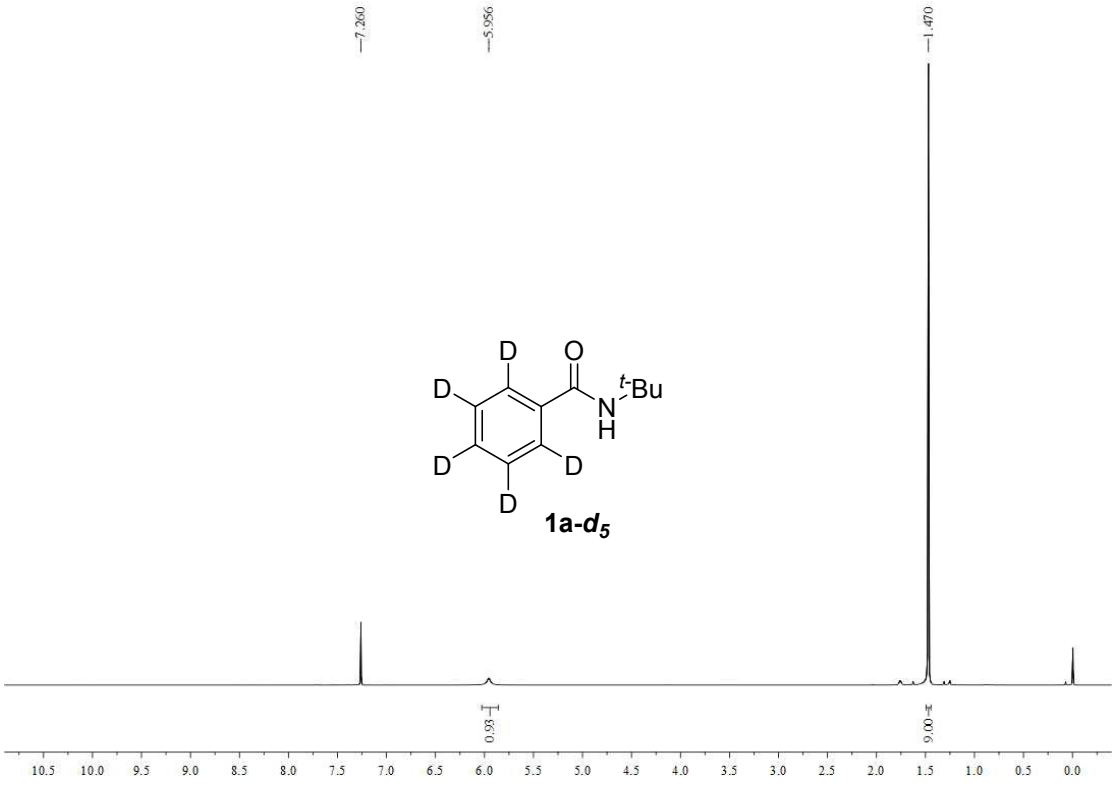


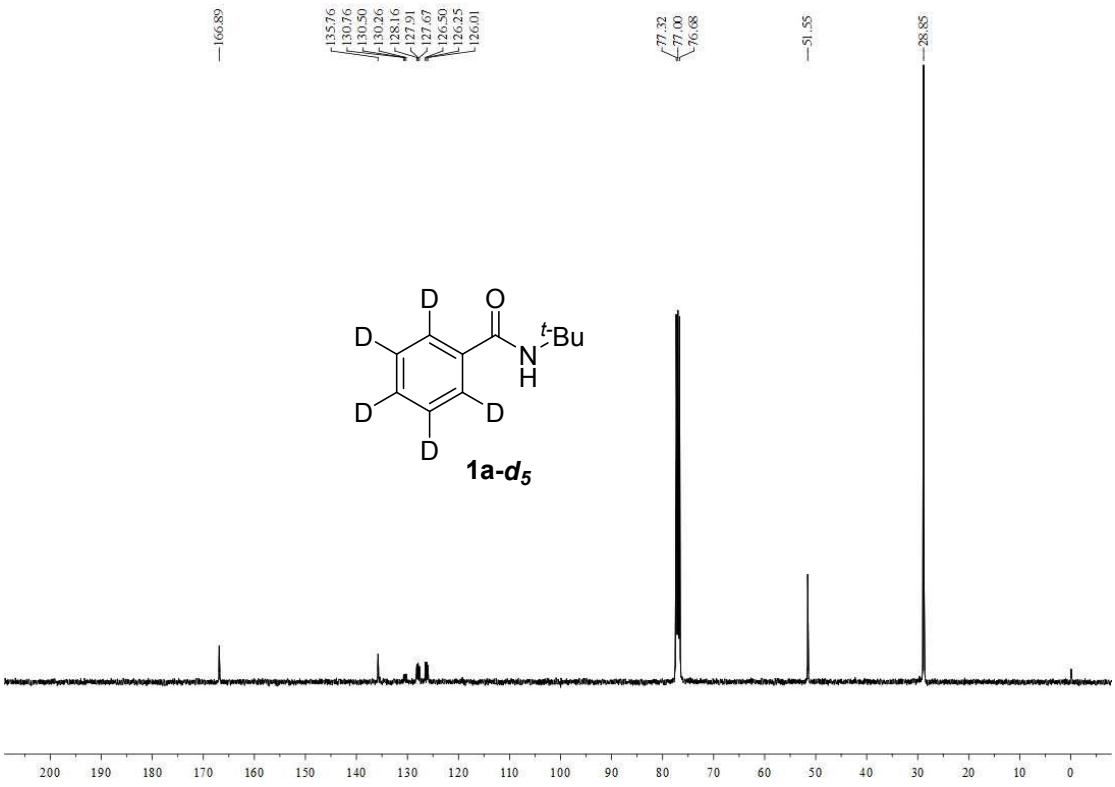
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1z



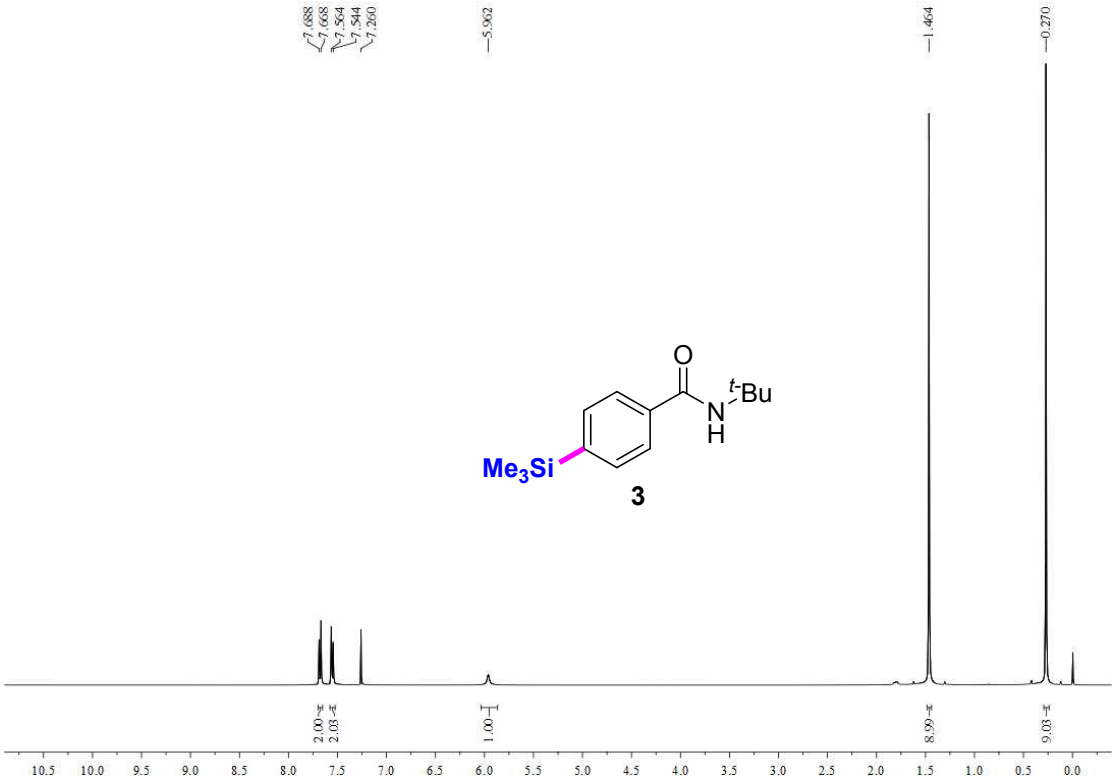


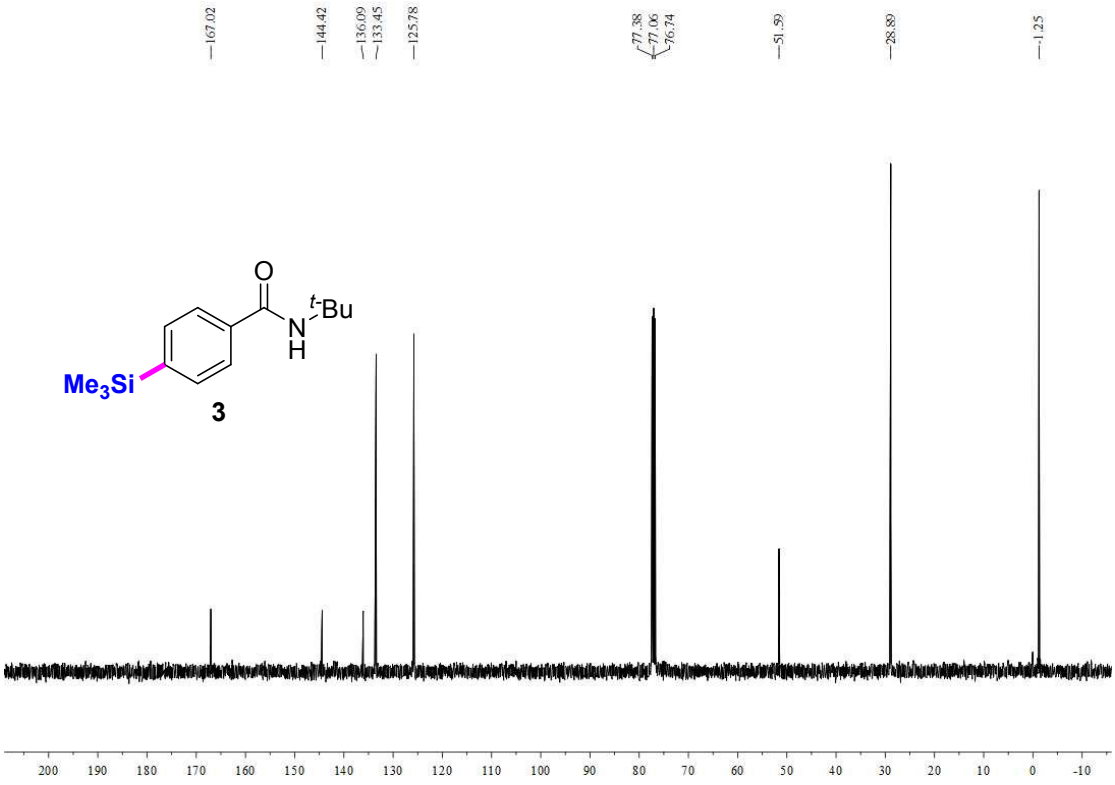
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1aa



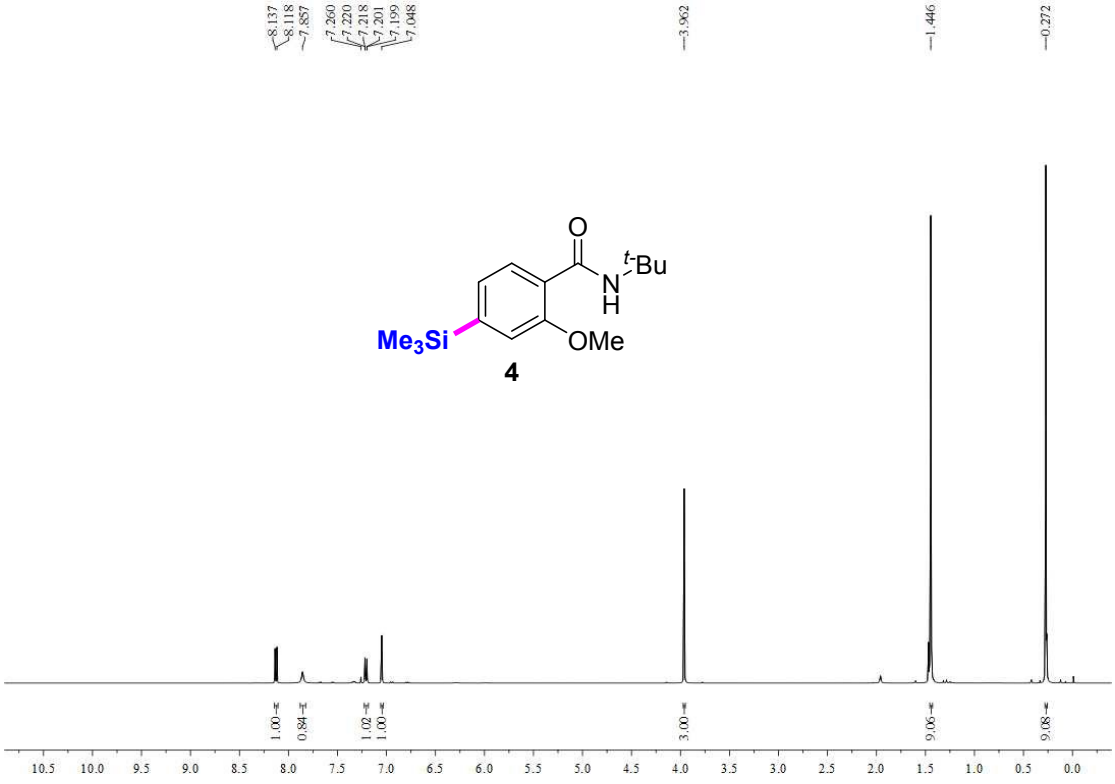


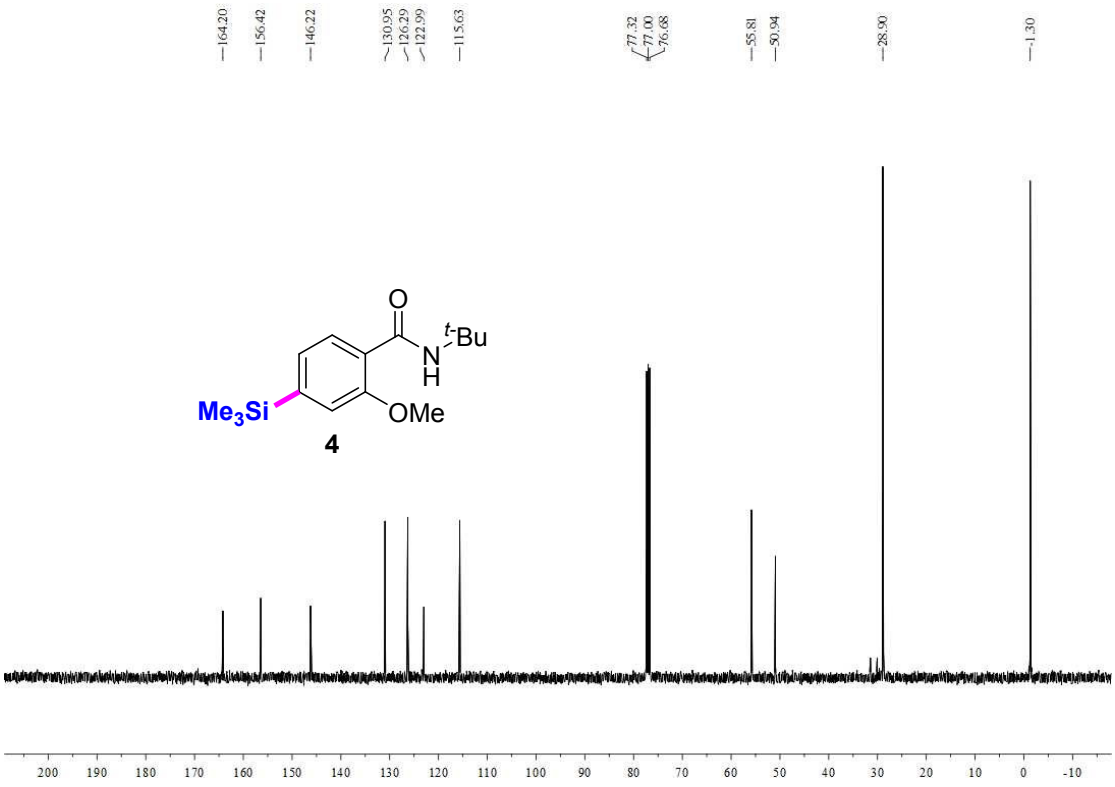
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1a-*d_5*



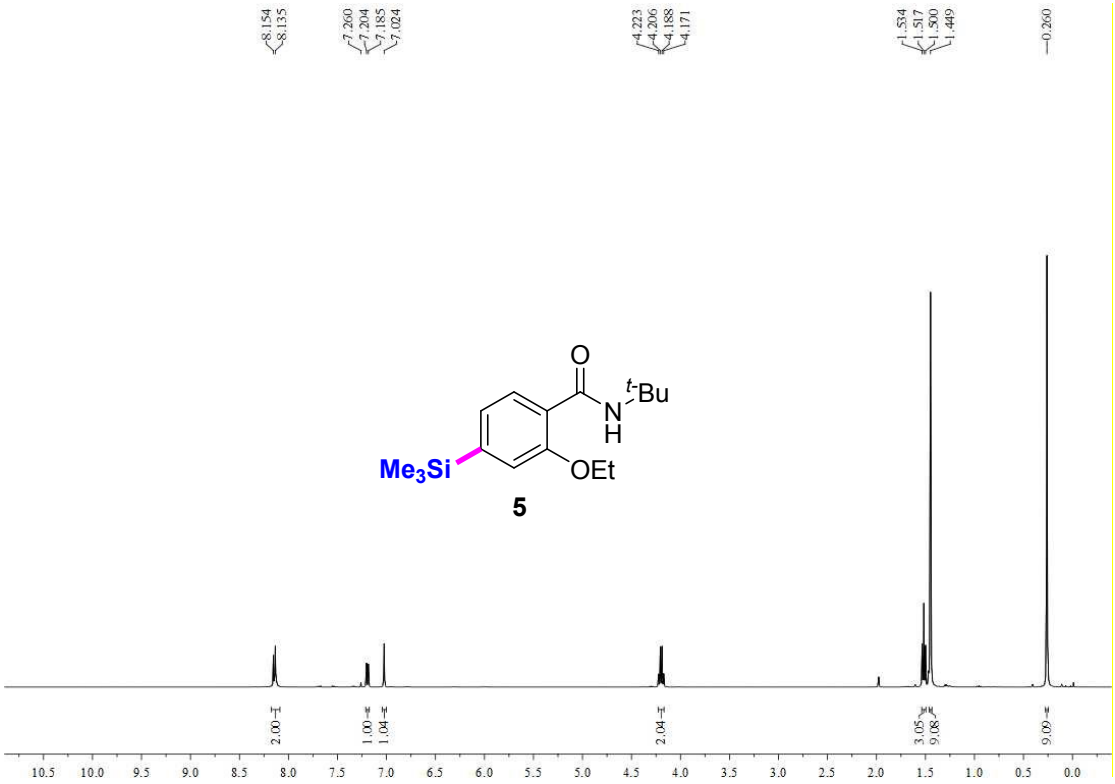


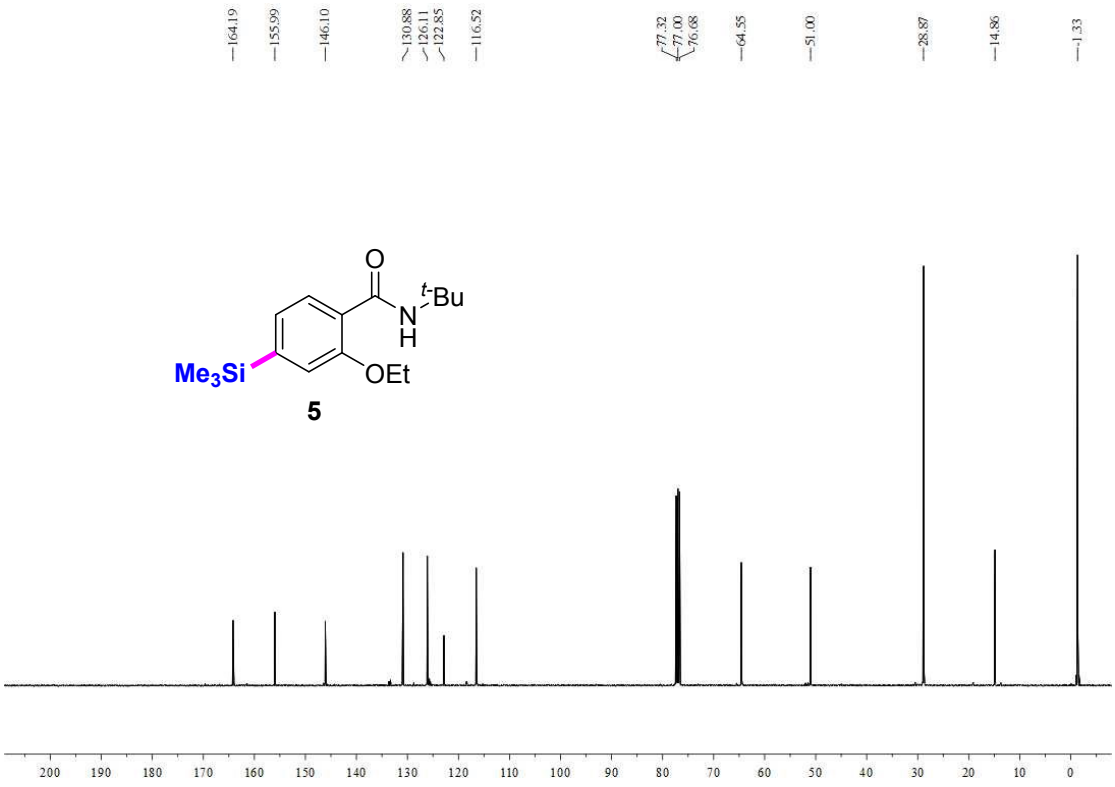
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3



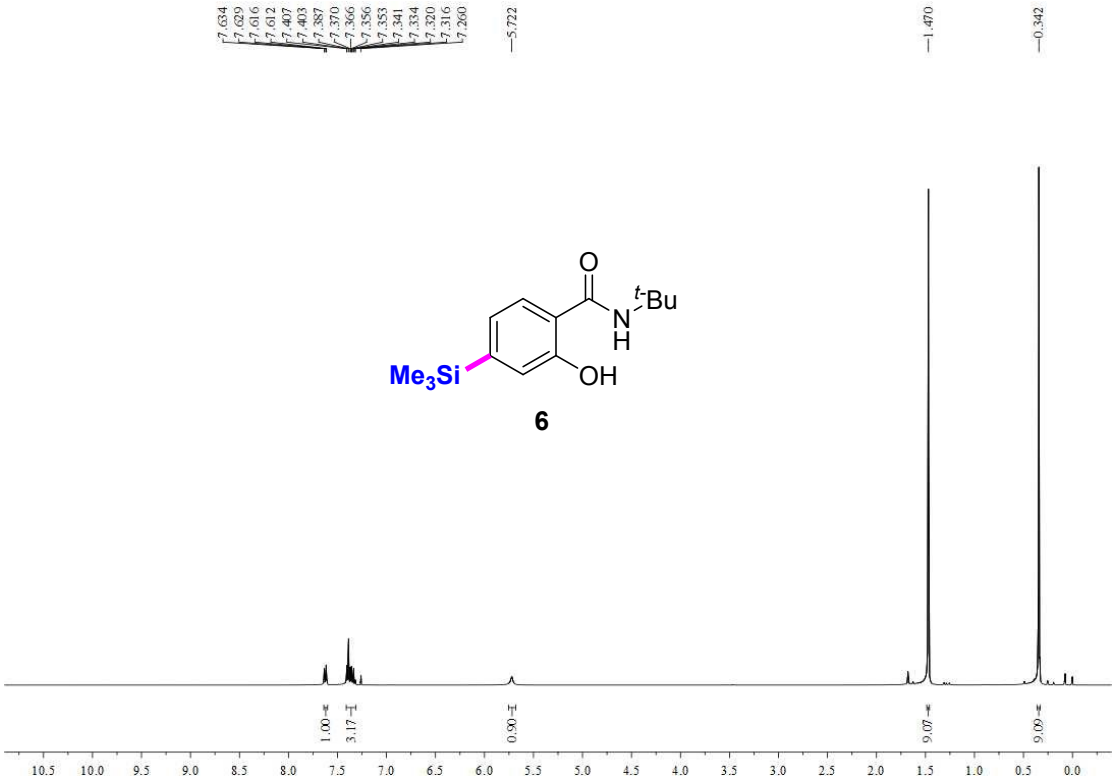


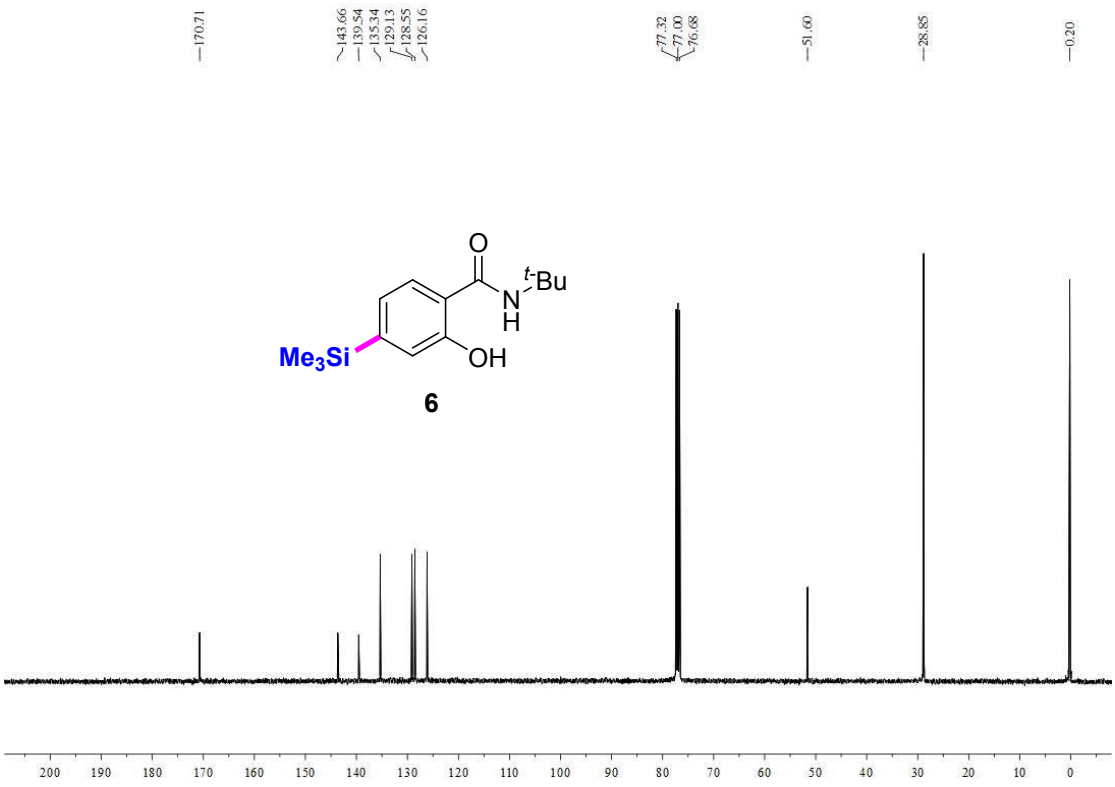
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 4



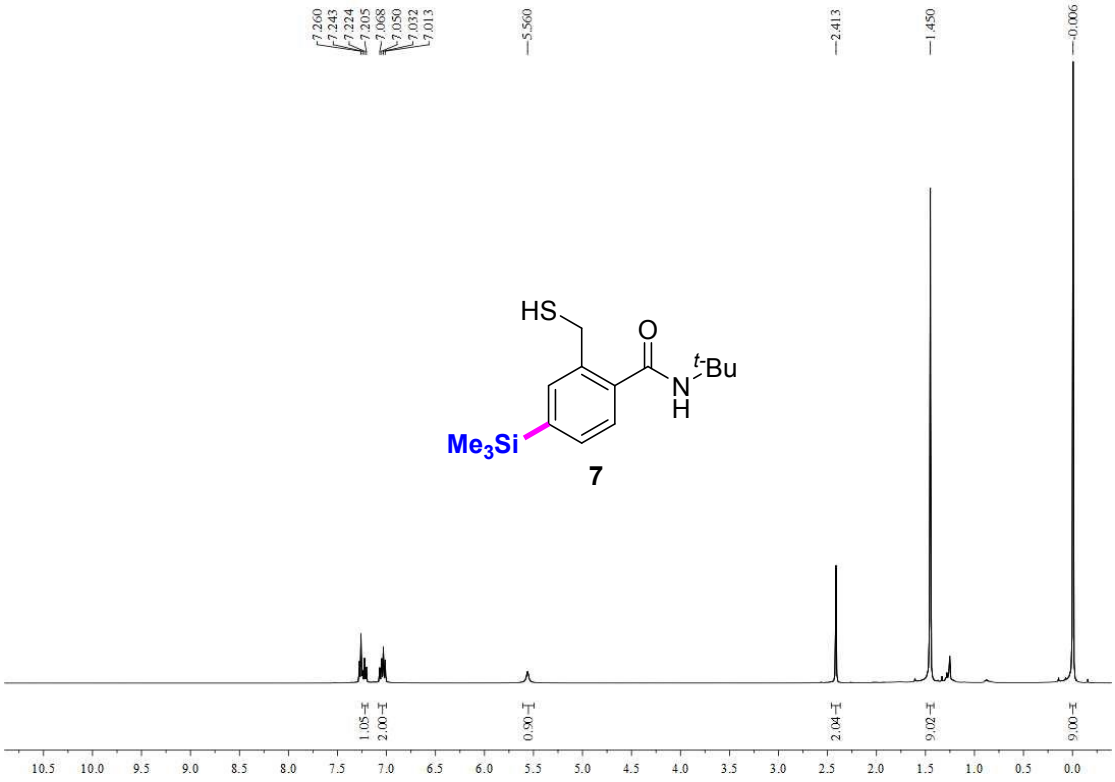


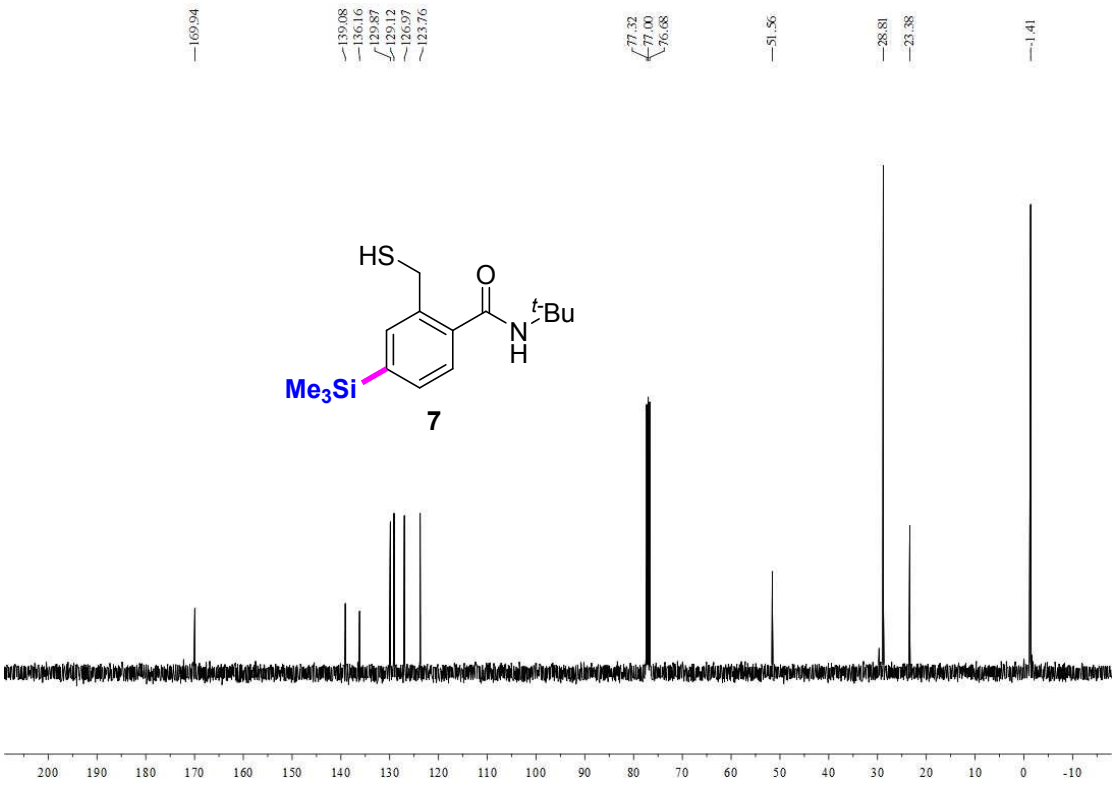
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 5



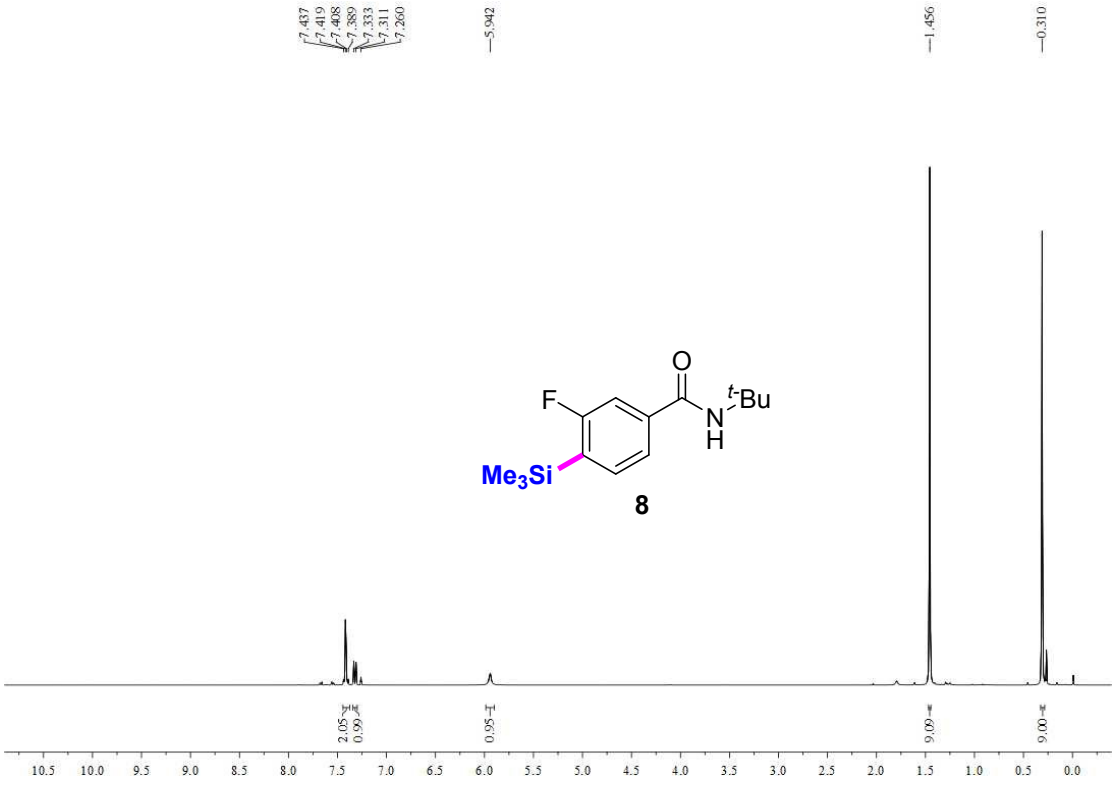


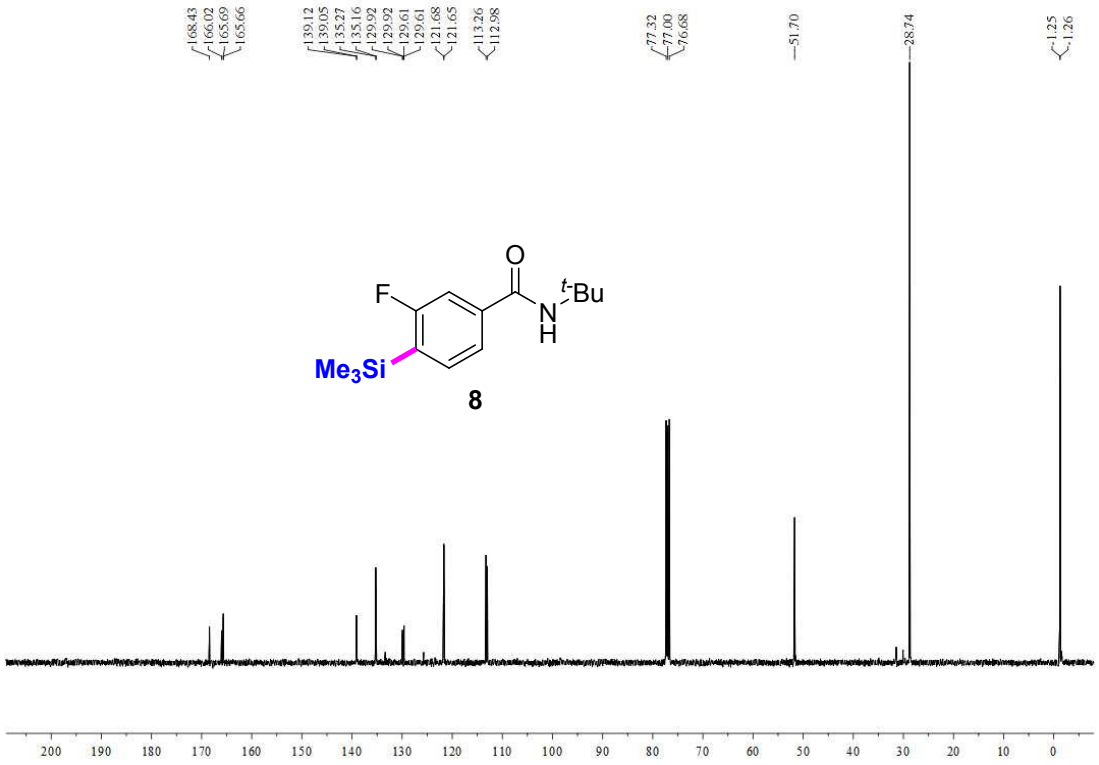
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 6



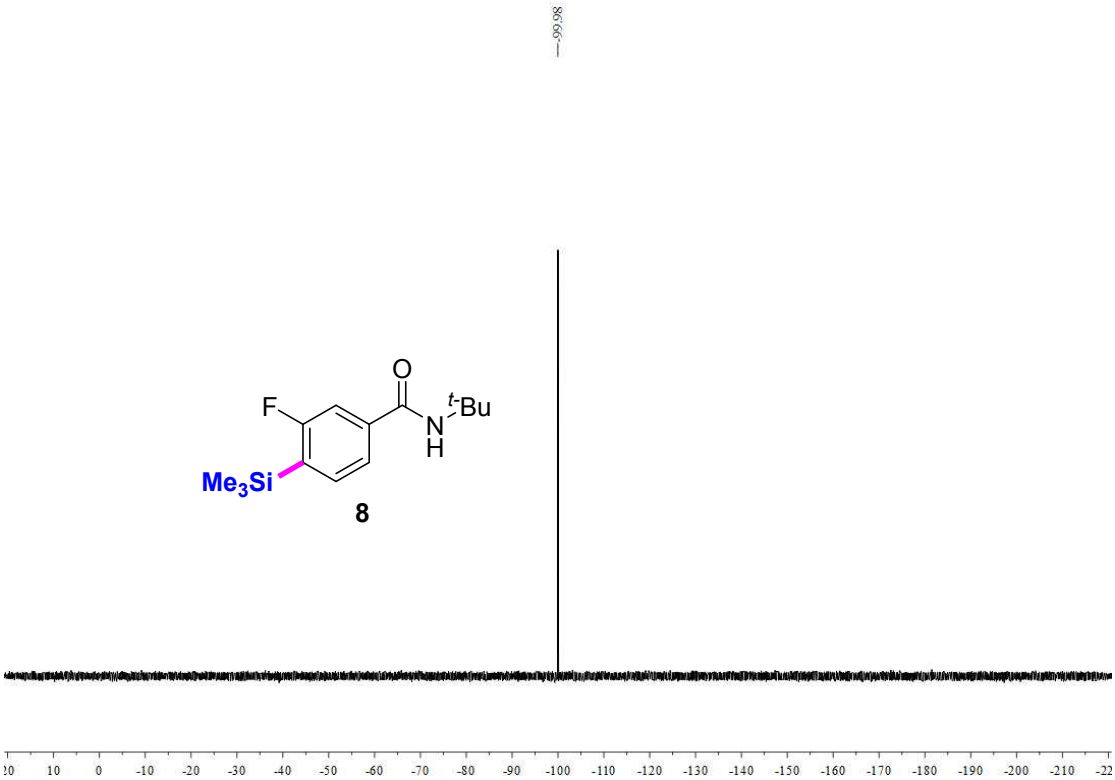


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 7

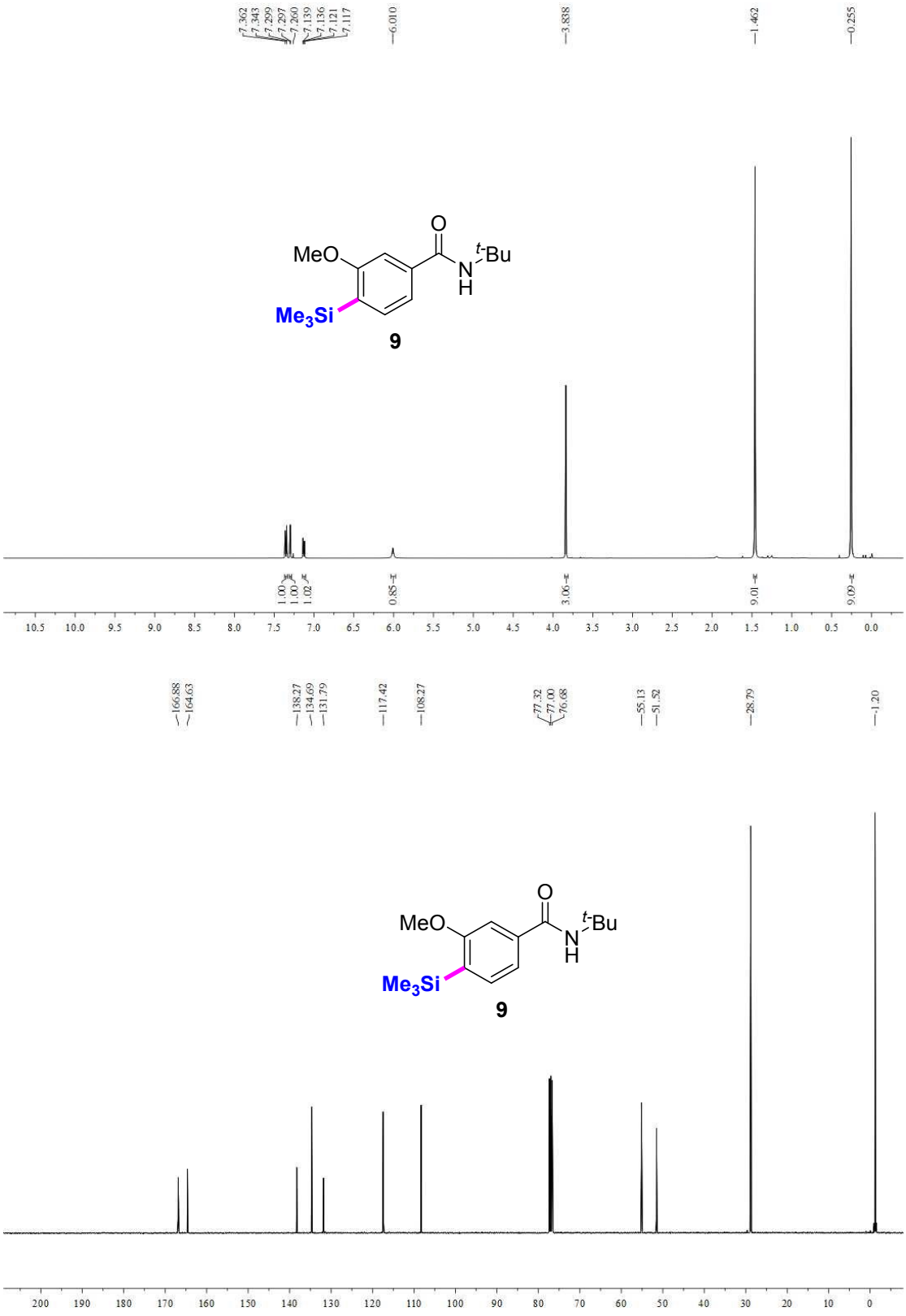




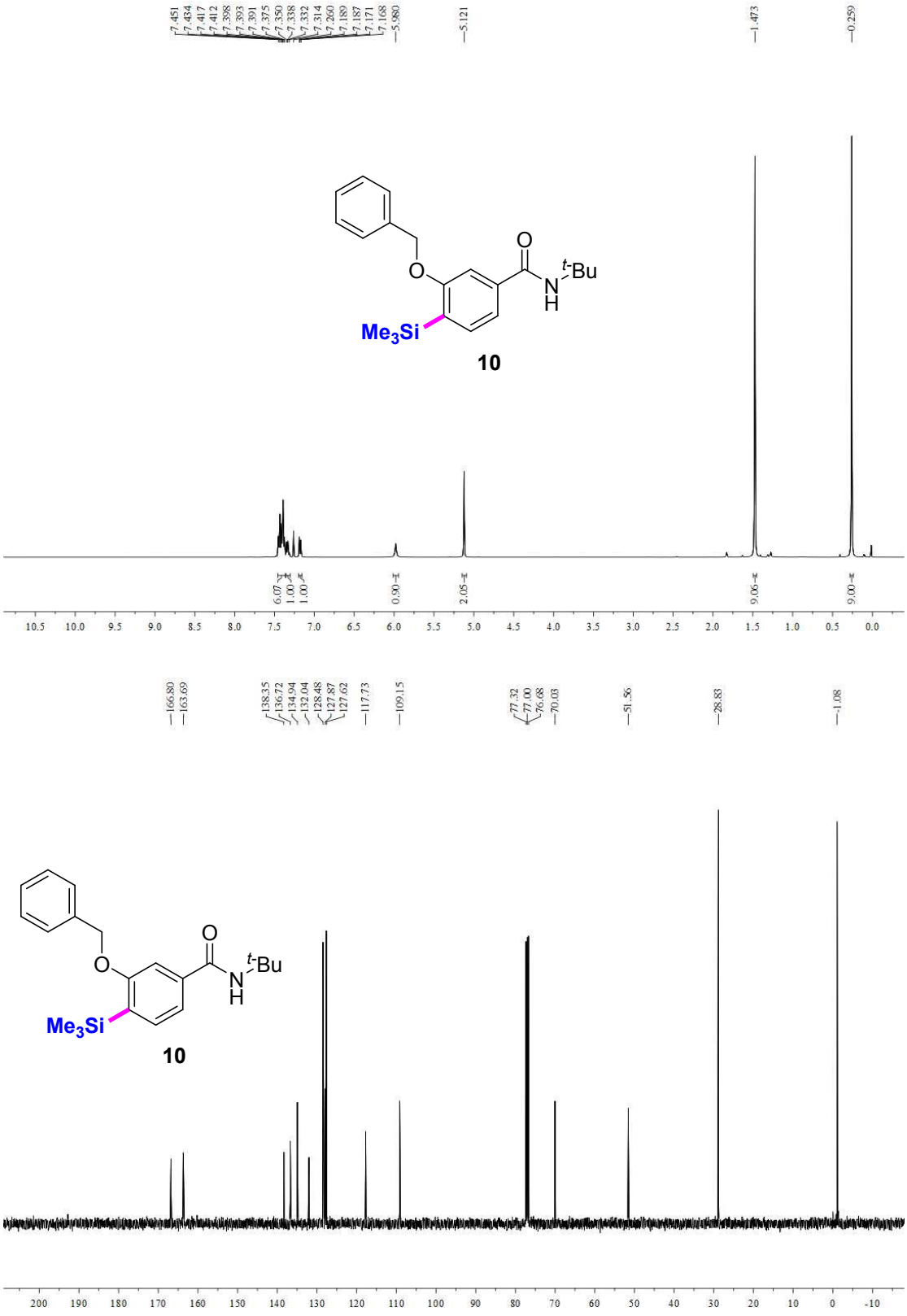
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 8



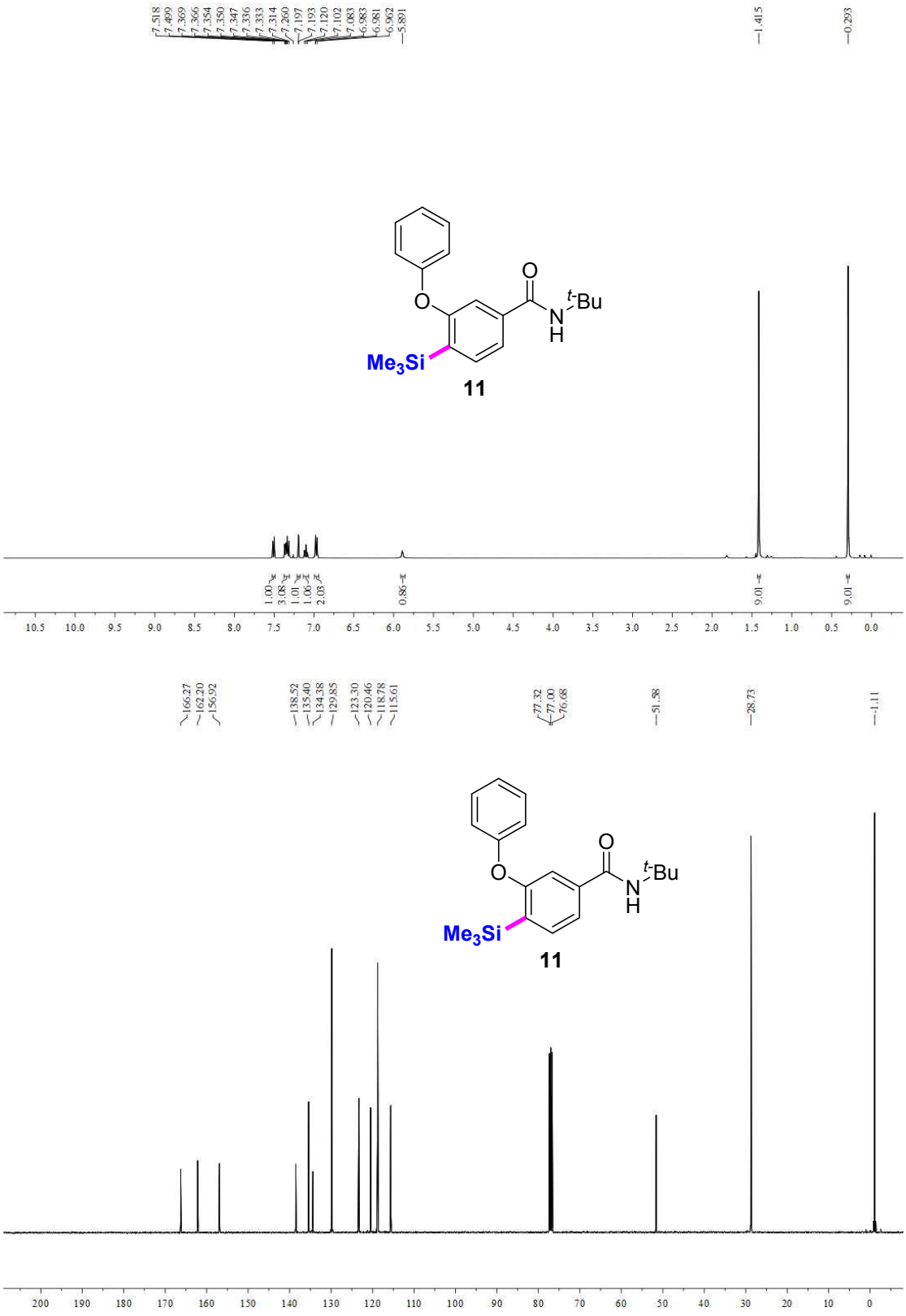
^{19}F NMR spectra in $CDCl_3$ for compound 8



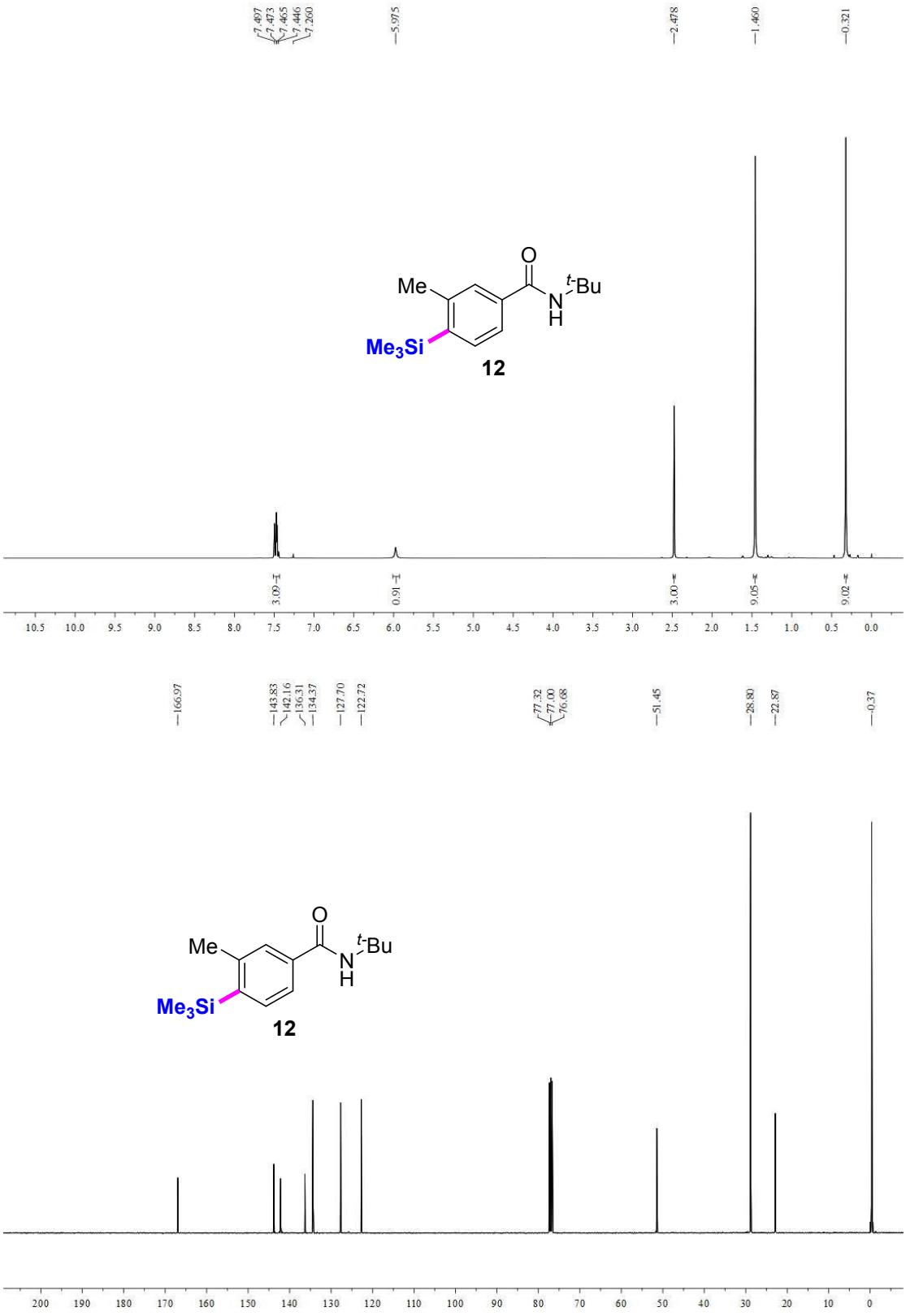
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 9



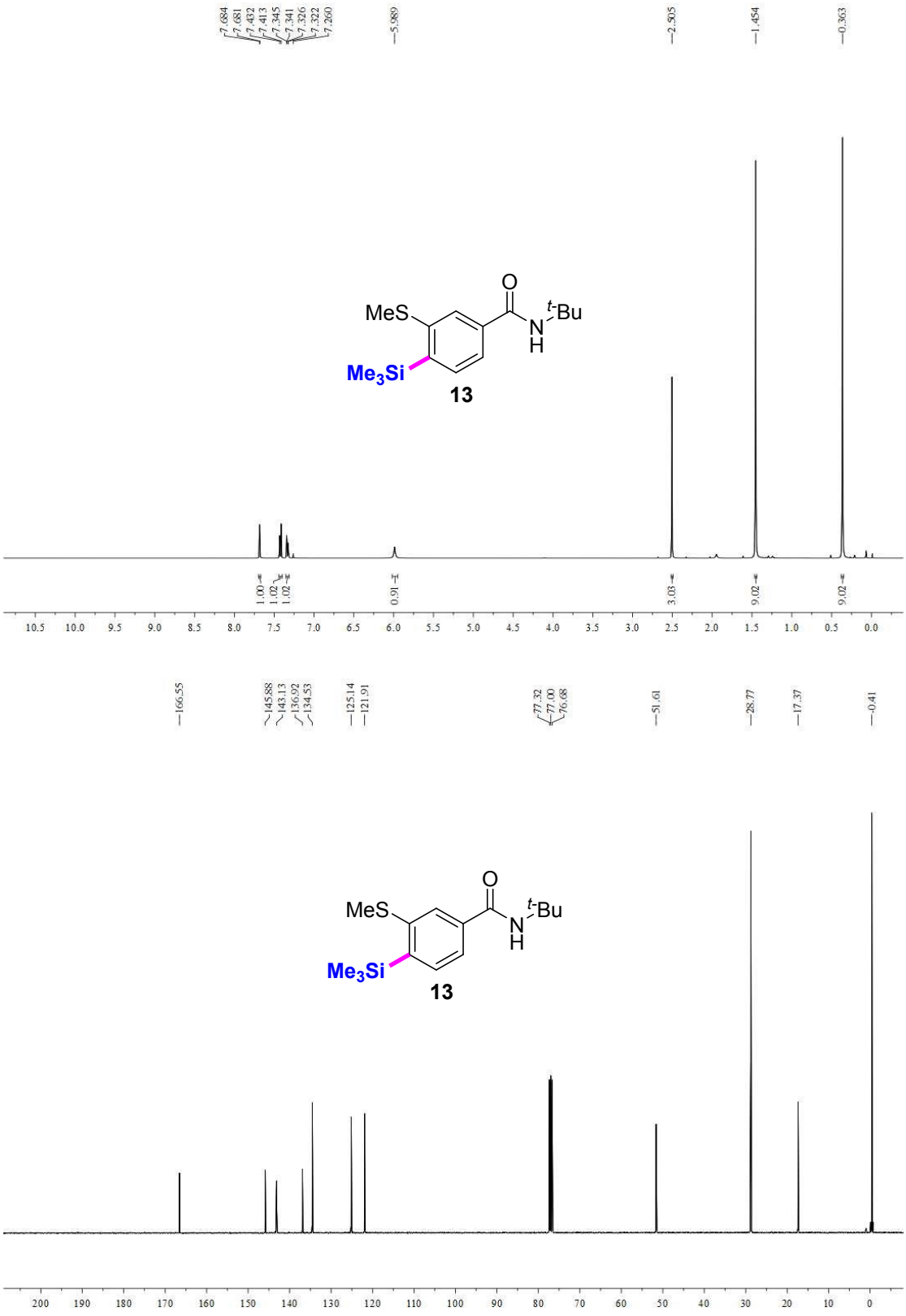
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 10



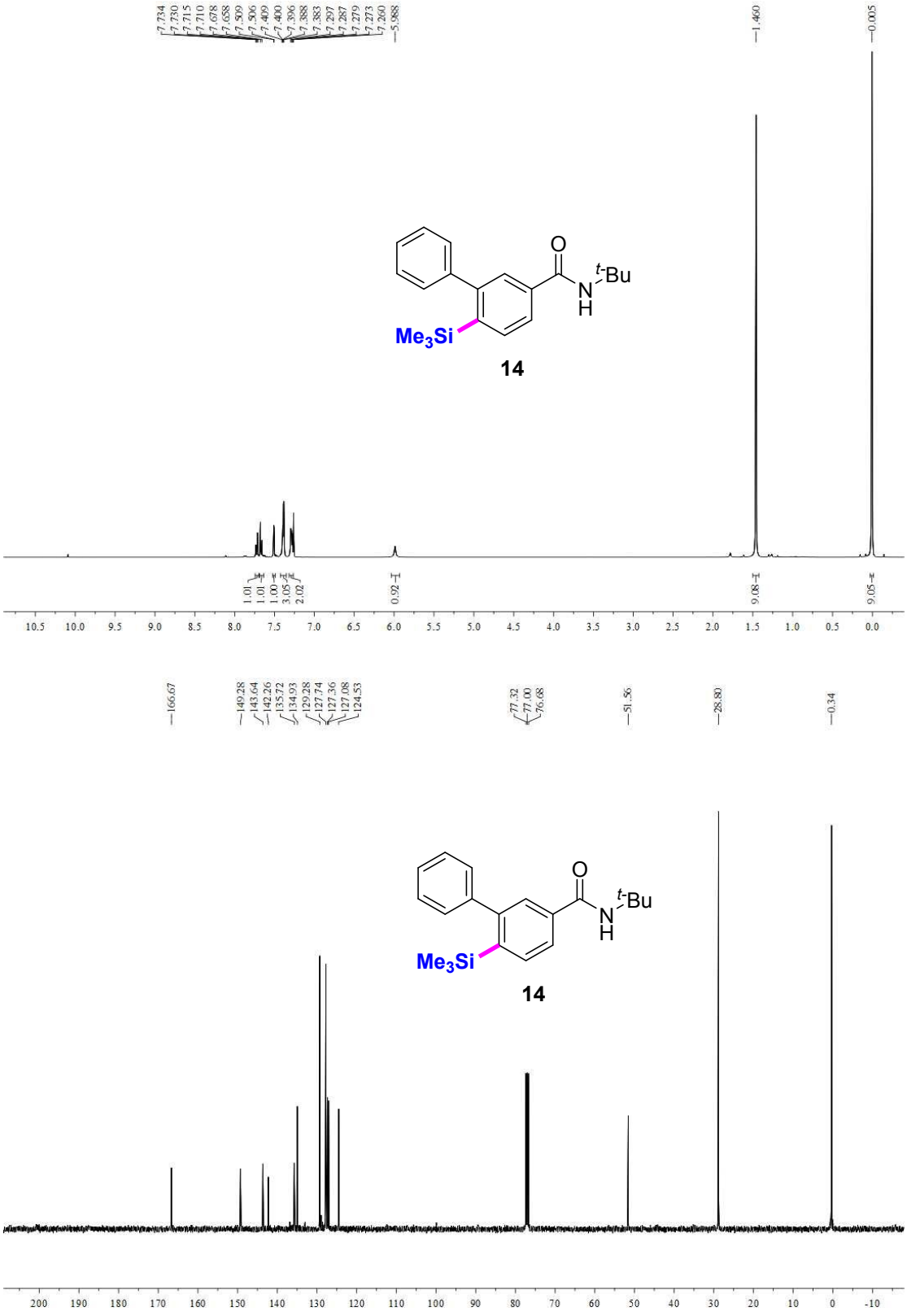
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 11



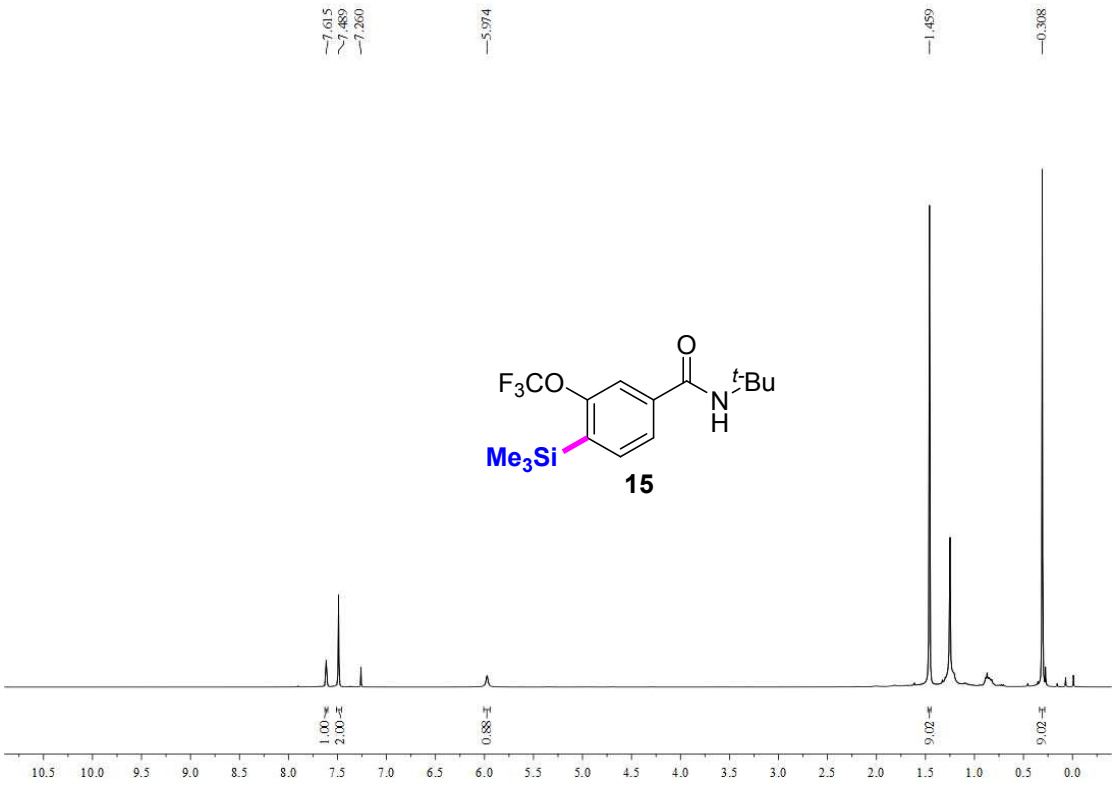
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 12

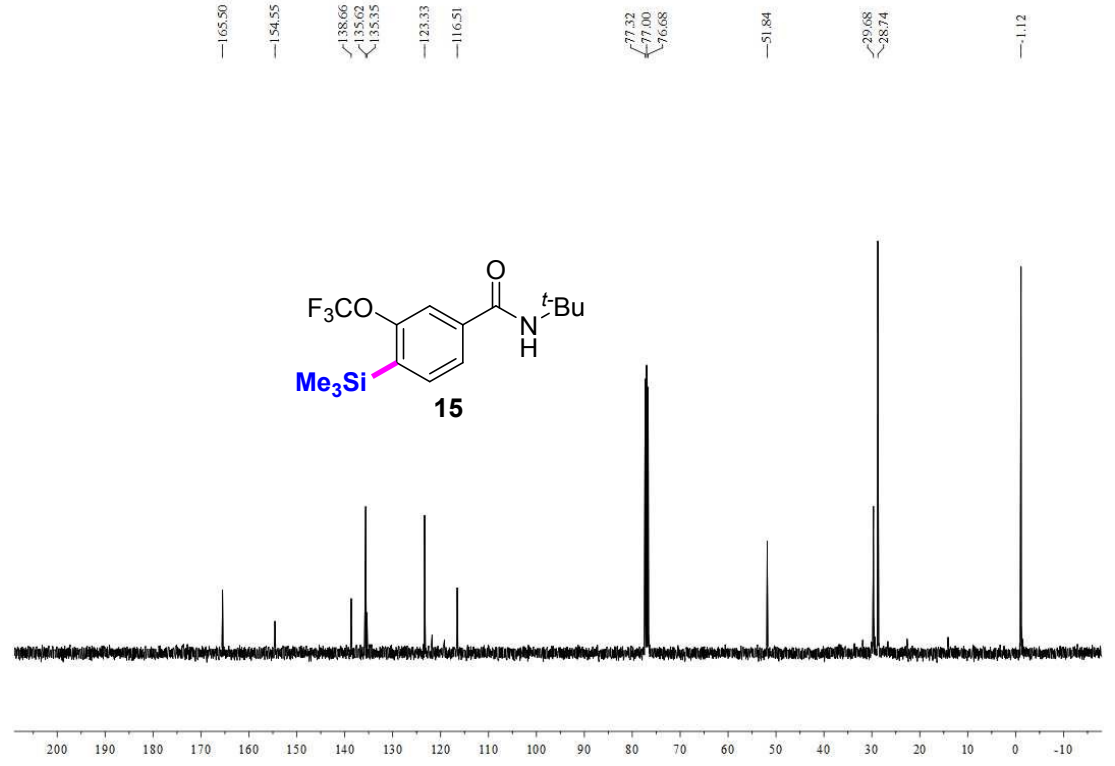


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 13

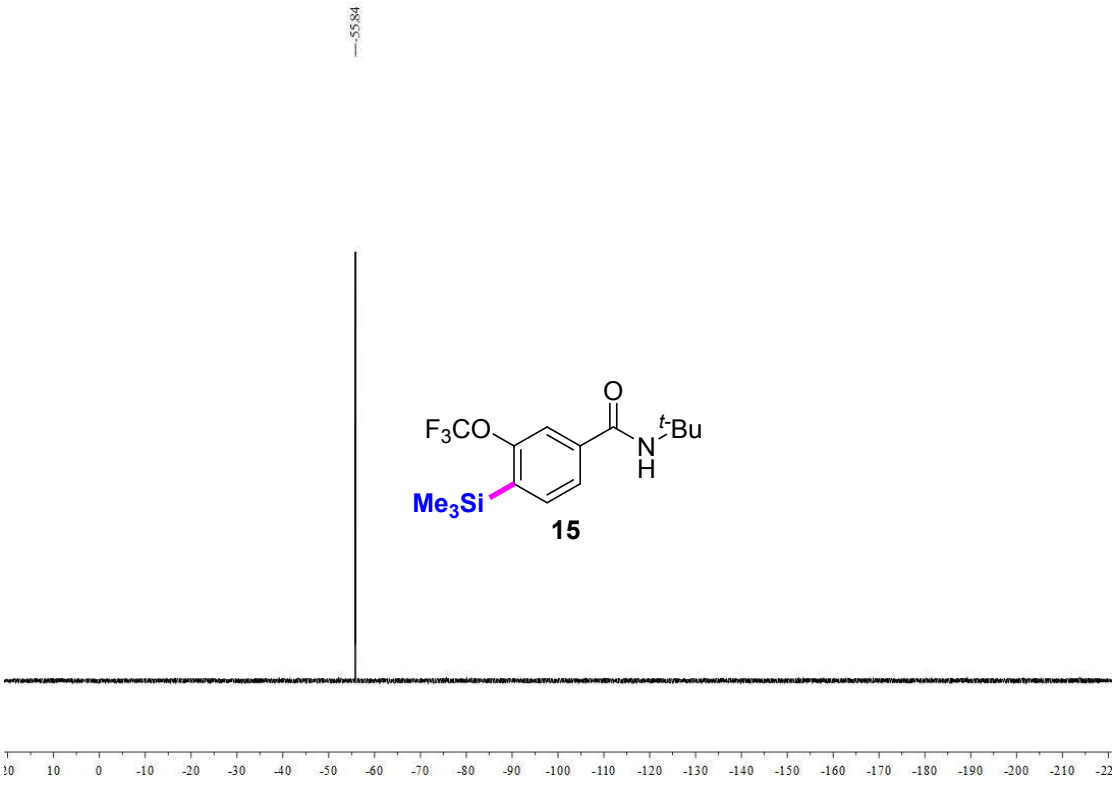


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 14

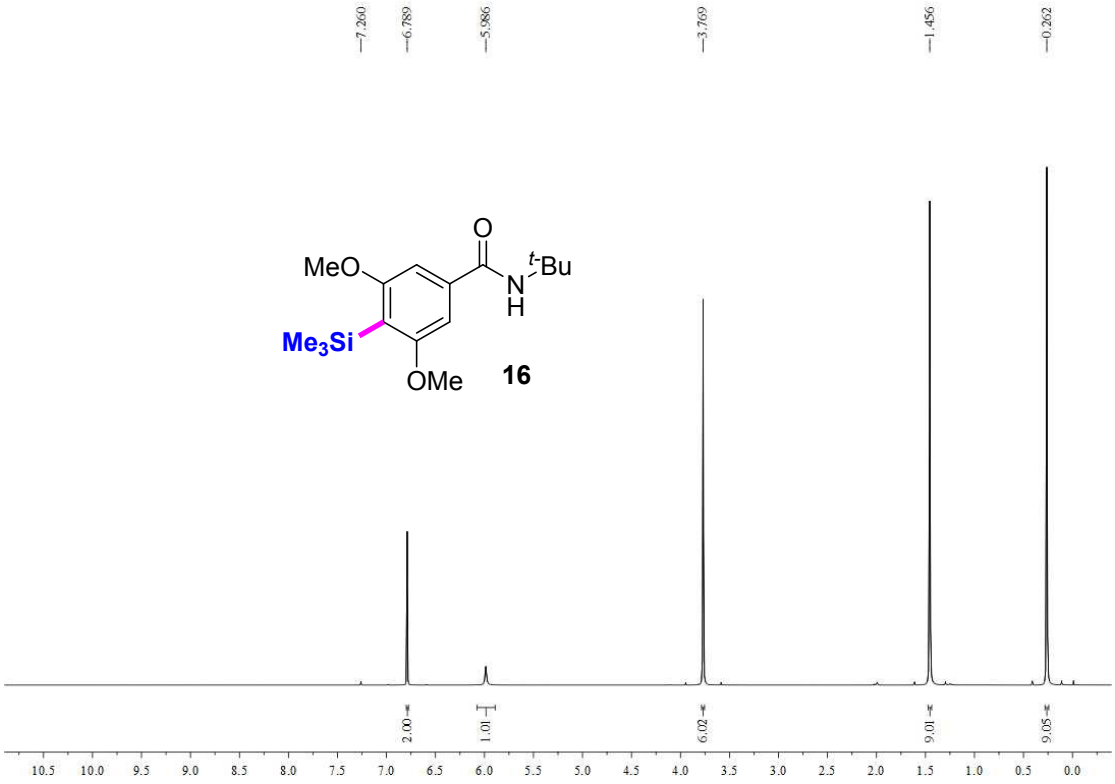


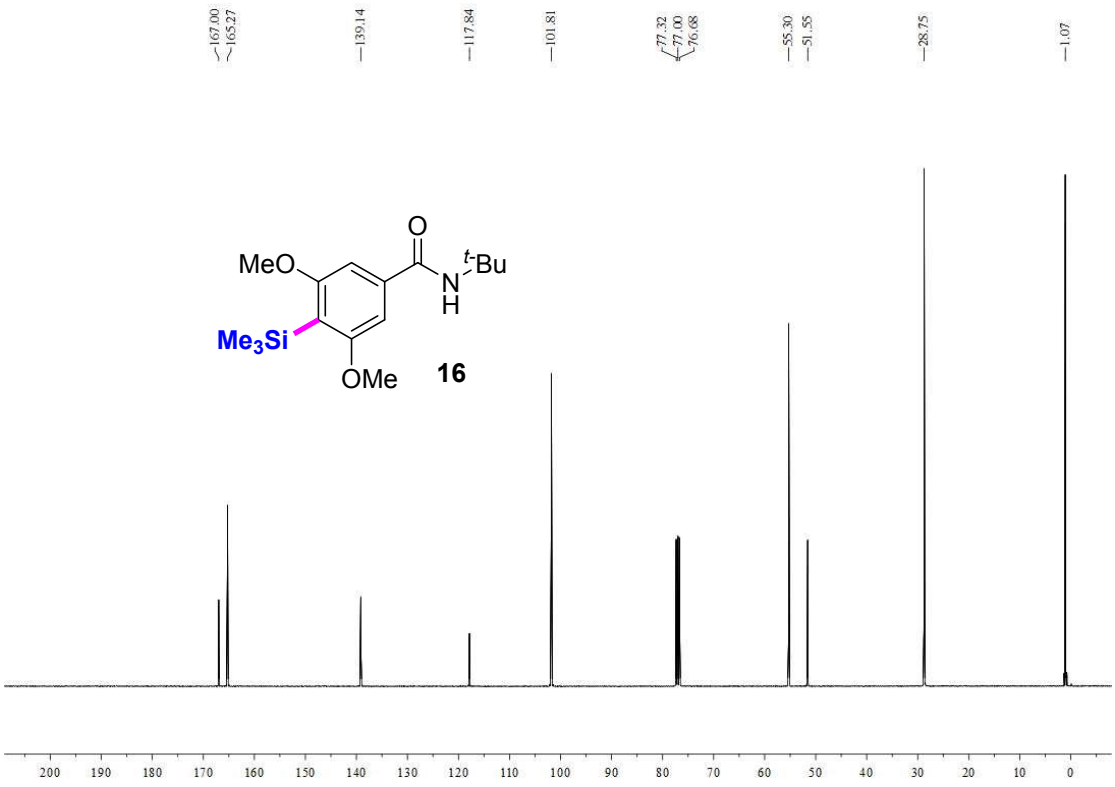


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 15

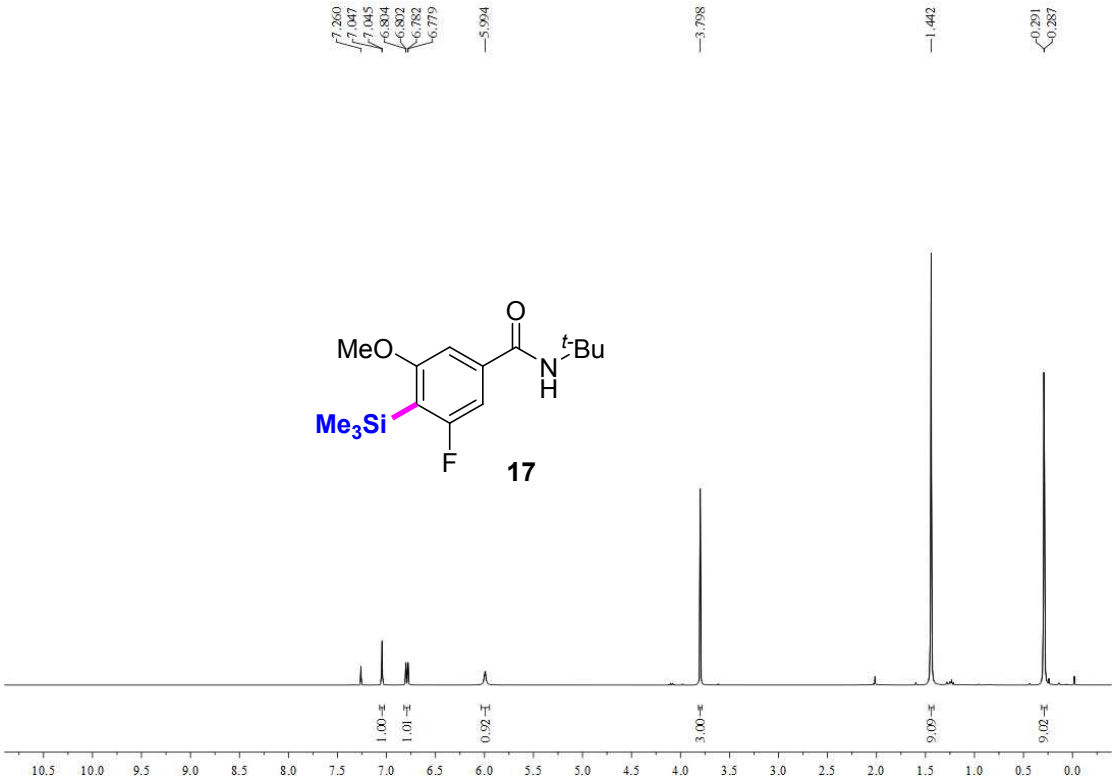


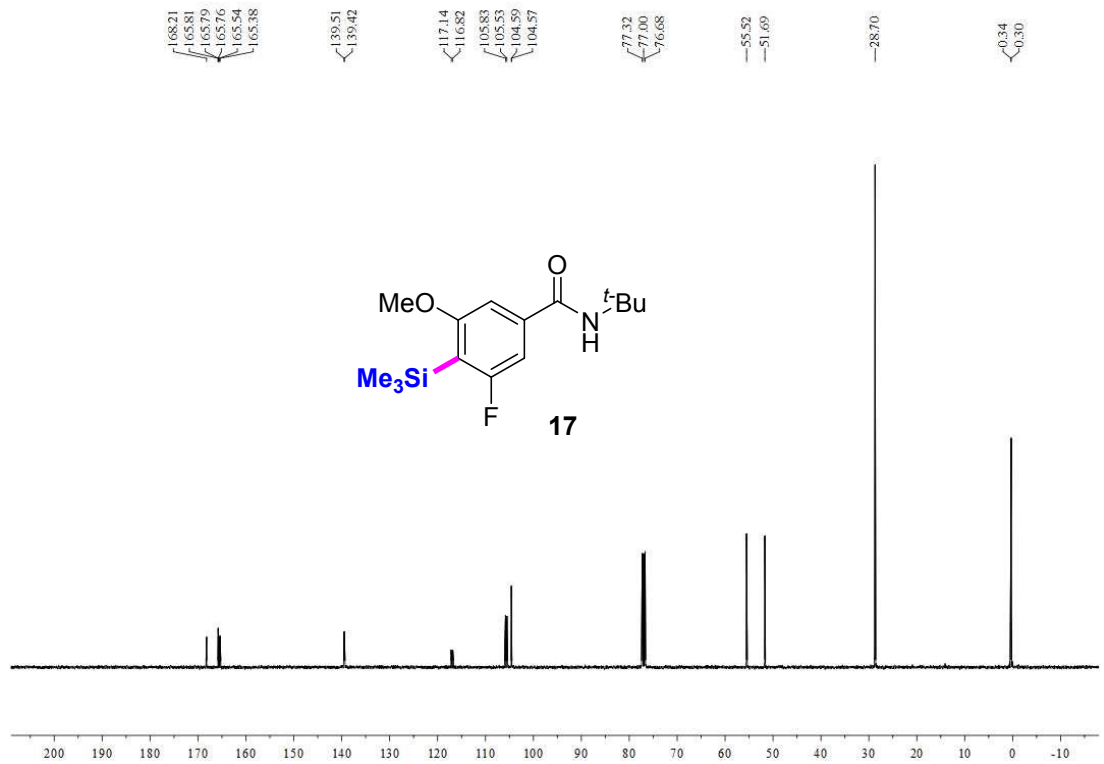
^{19}F NMR spectra in $CDCl_3$ for compound 15



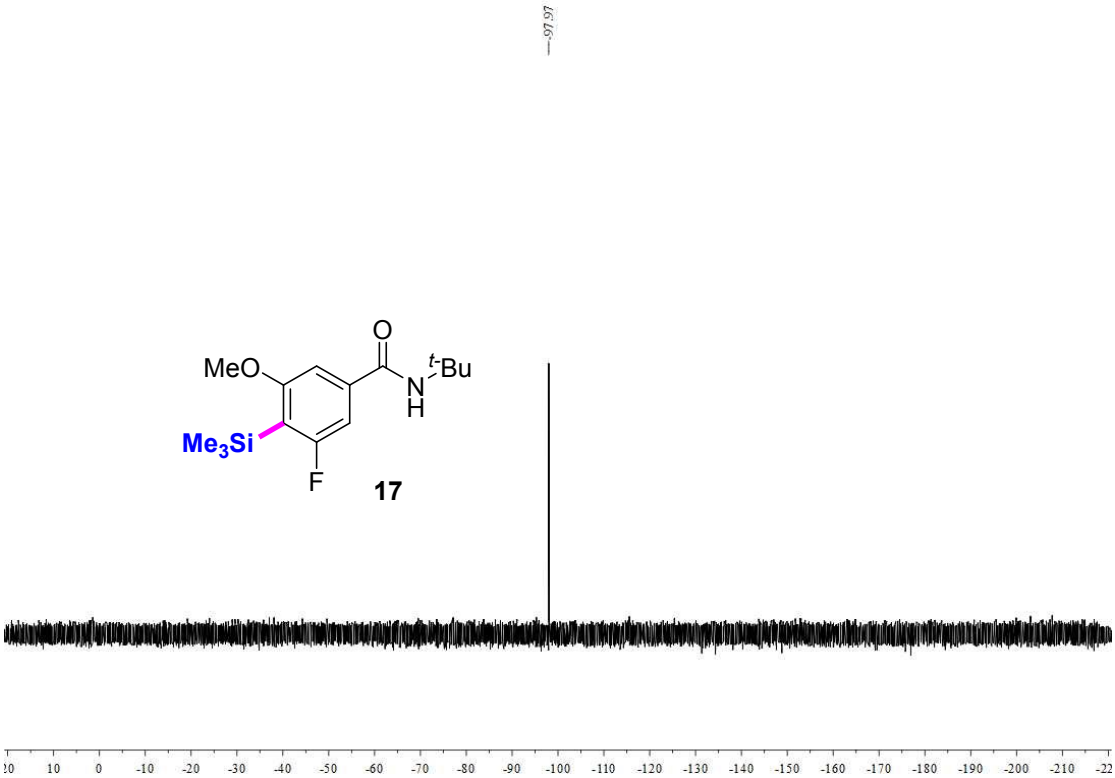


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 16

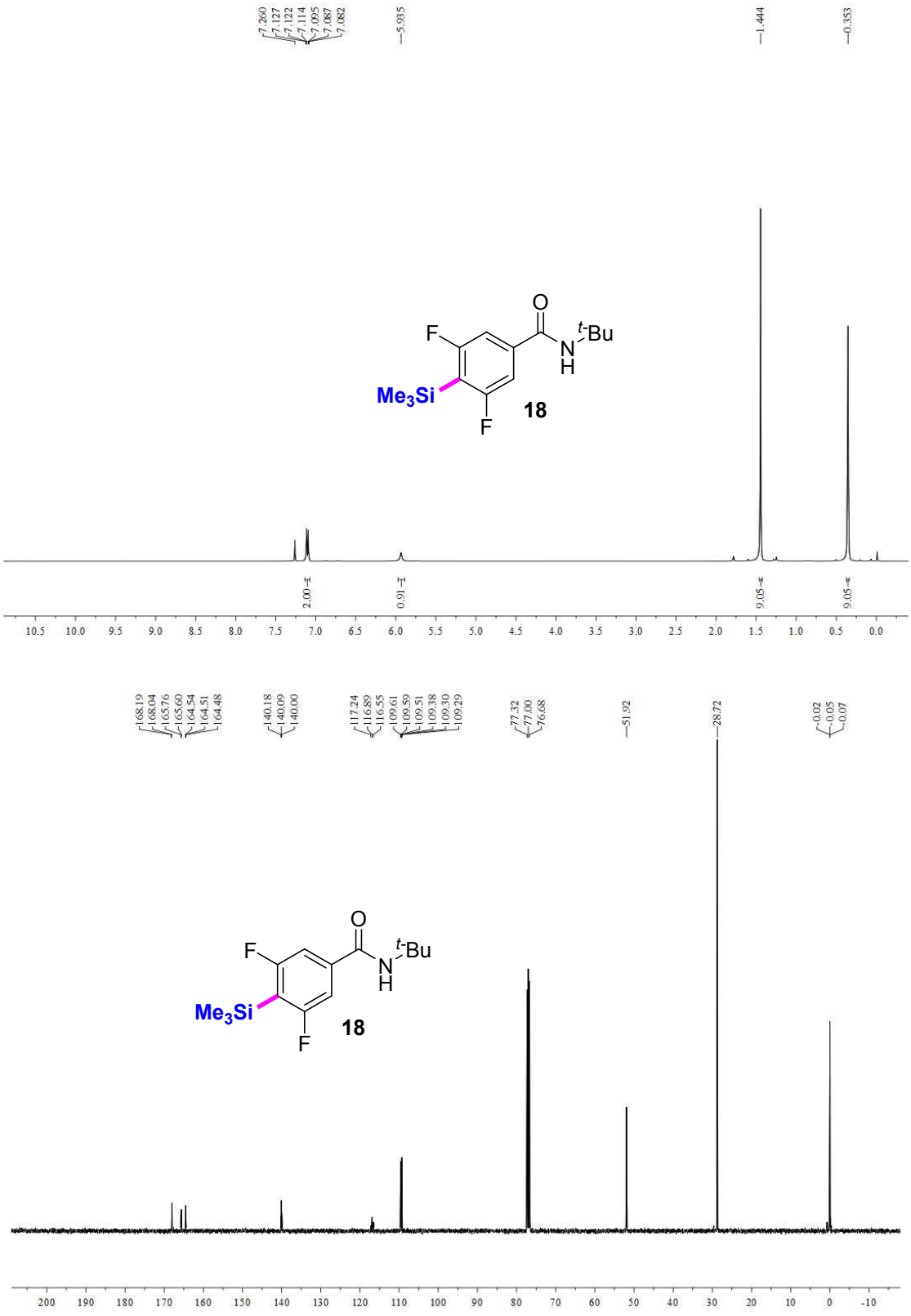




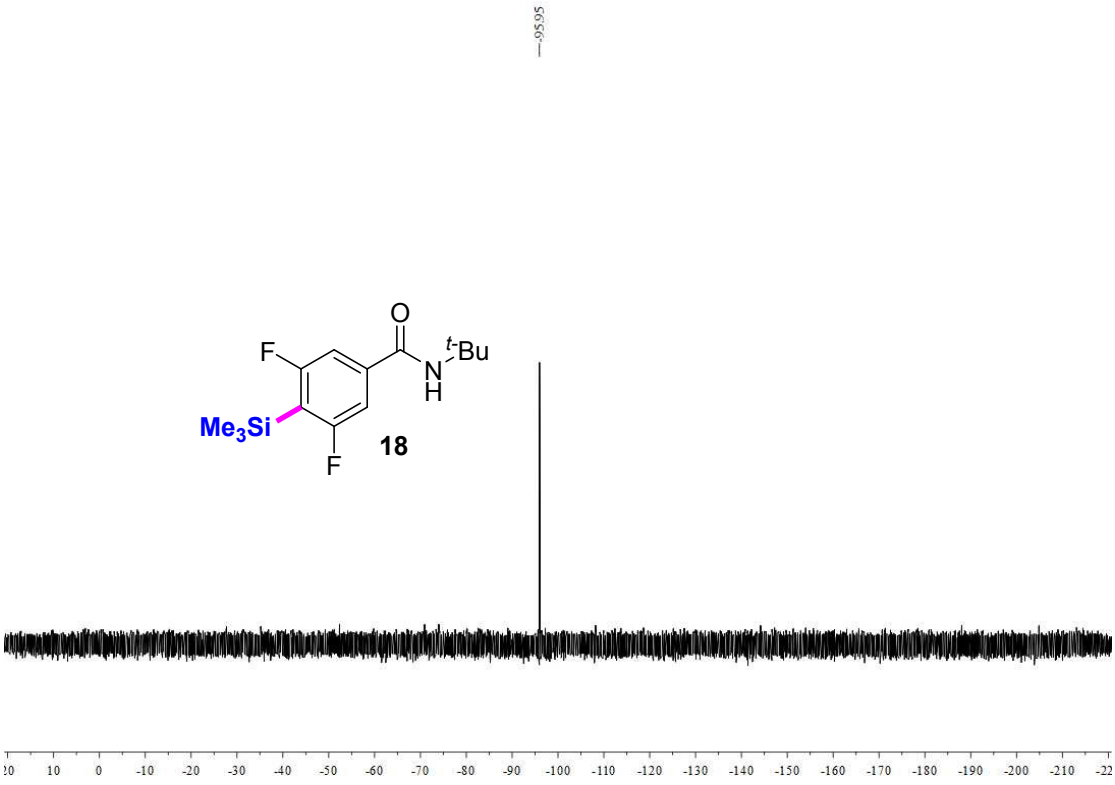
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 17



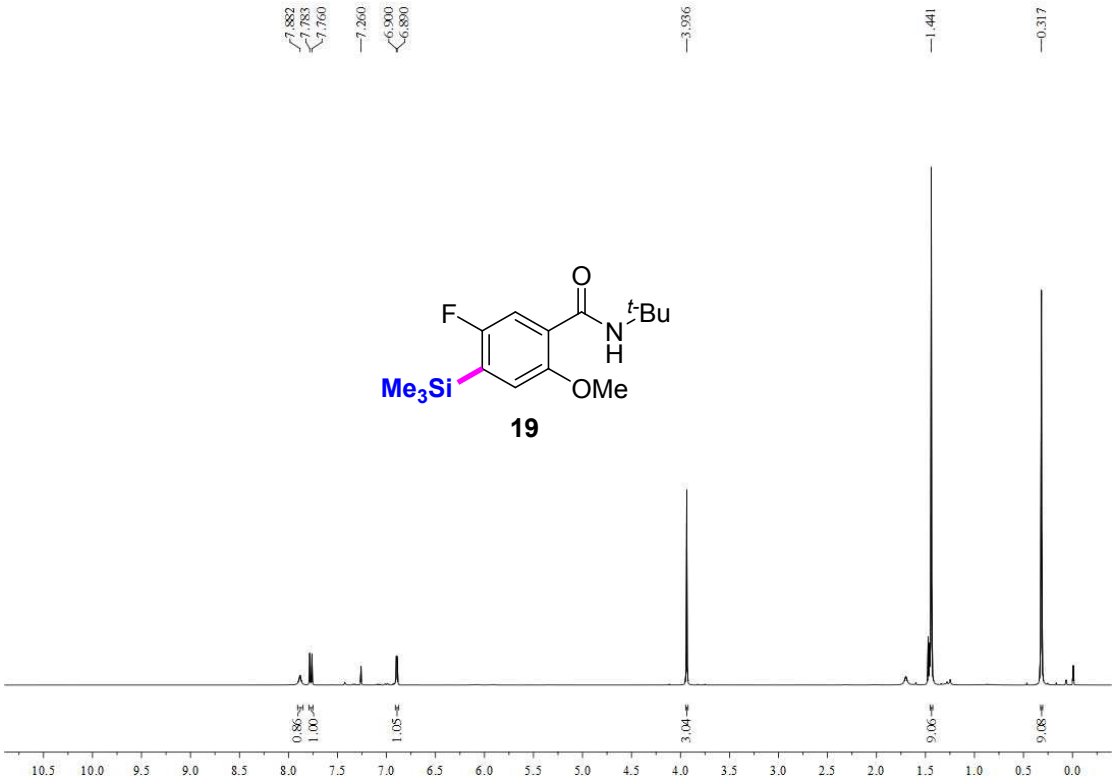
^{19}F NMR spectra in $CDCl_3$ for compound 17

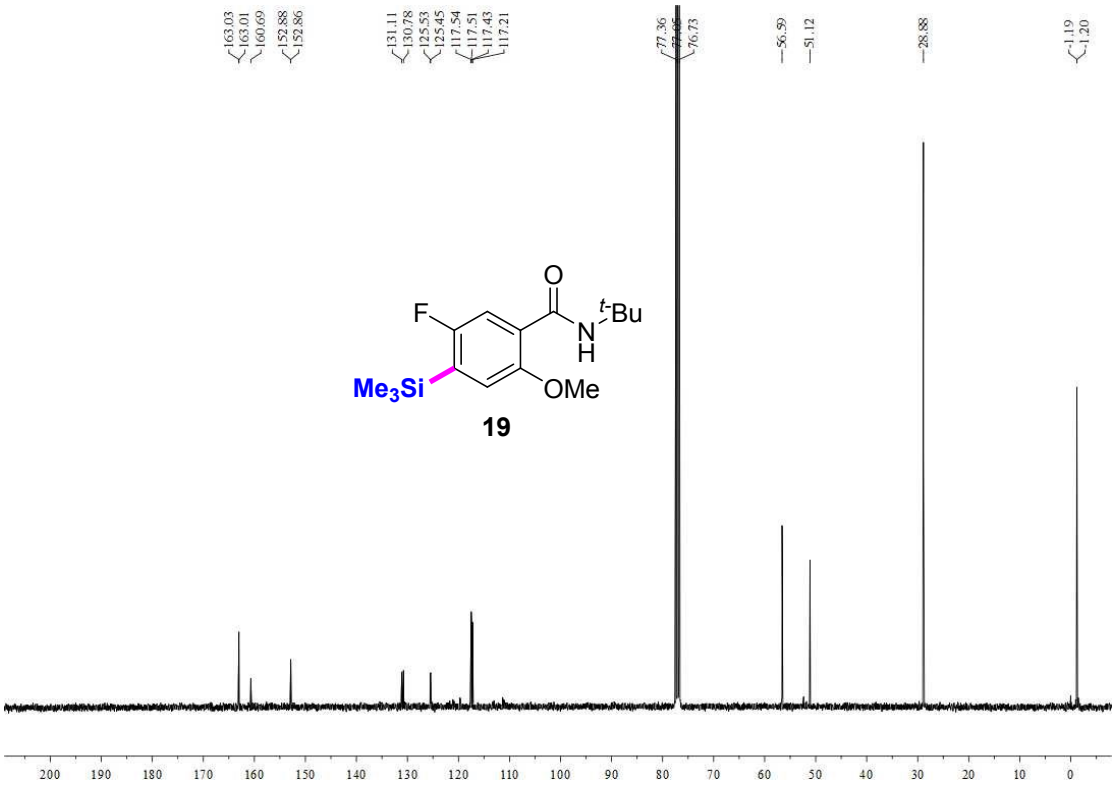


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 18

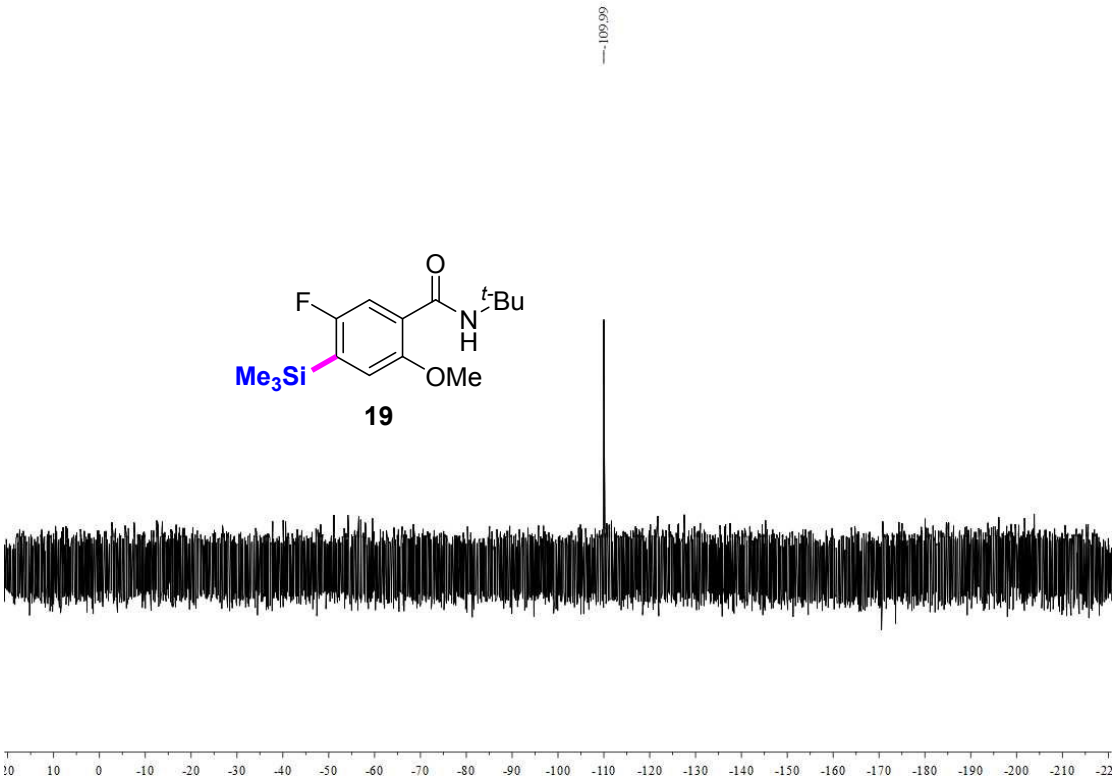


^{19}F NMR spectra in $CDCl_3$ for compound 18

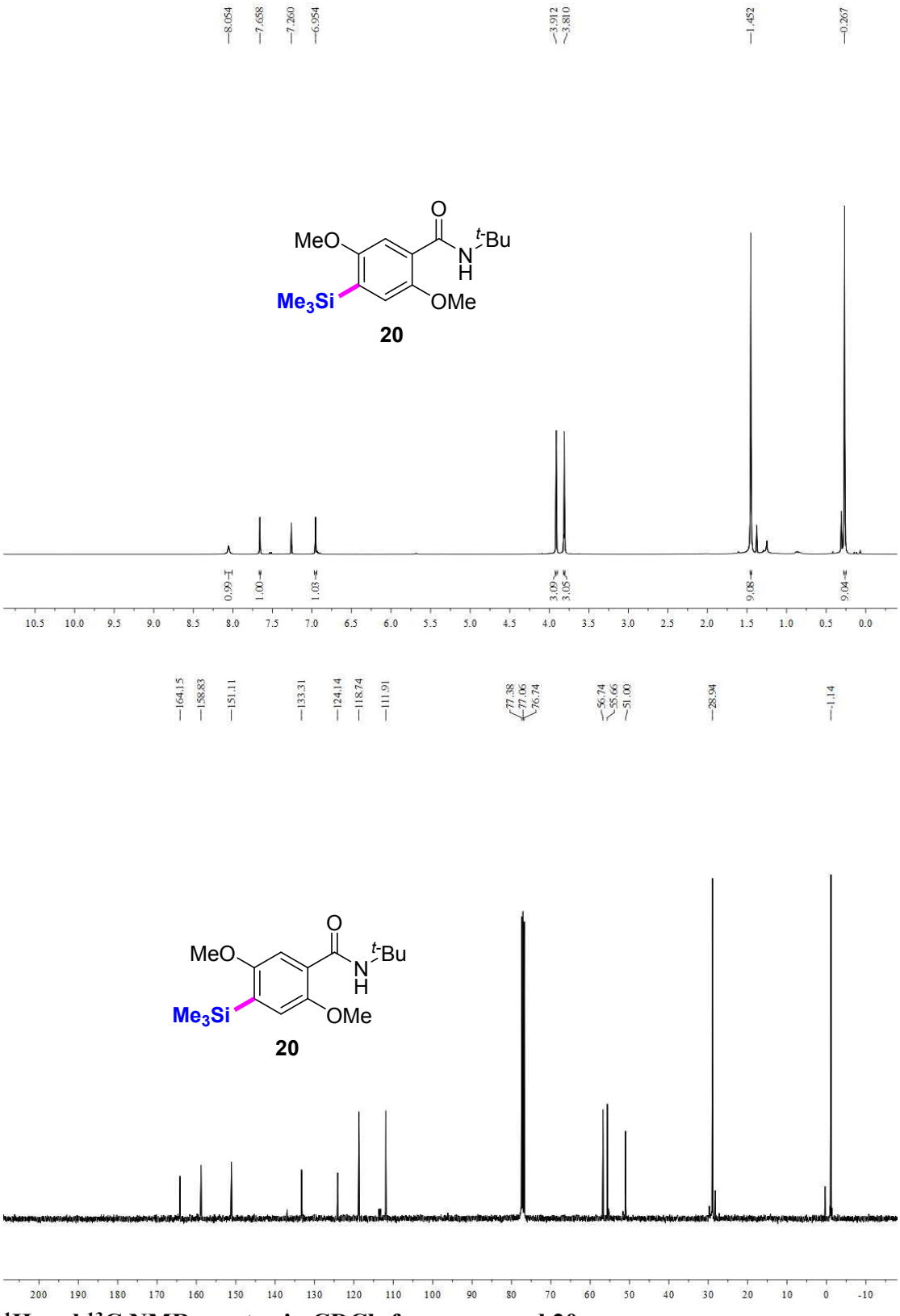




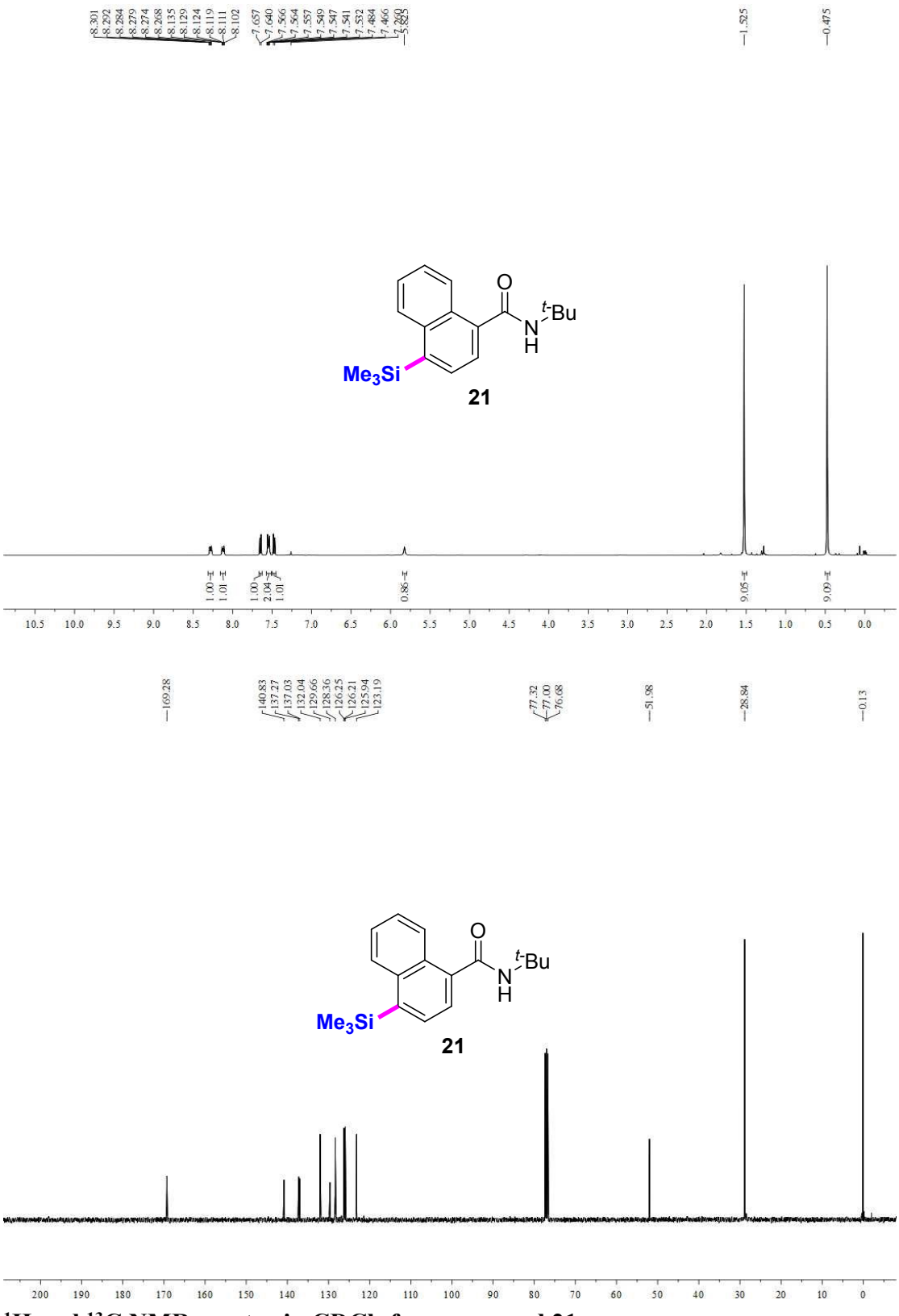
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 19



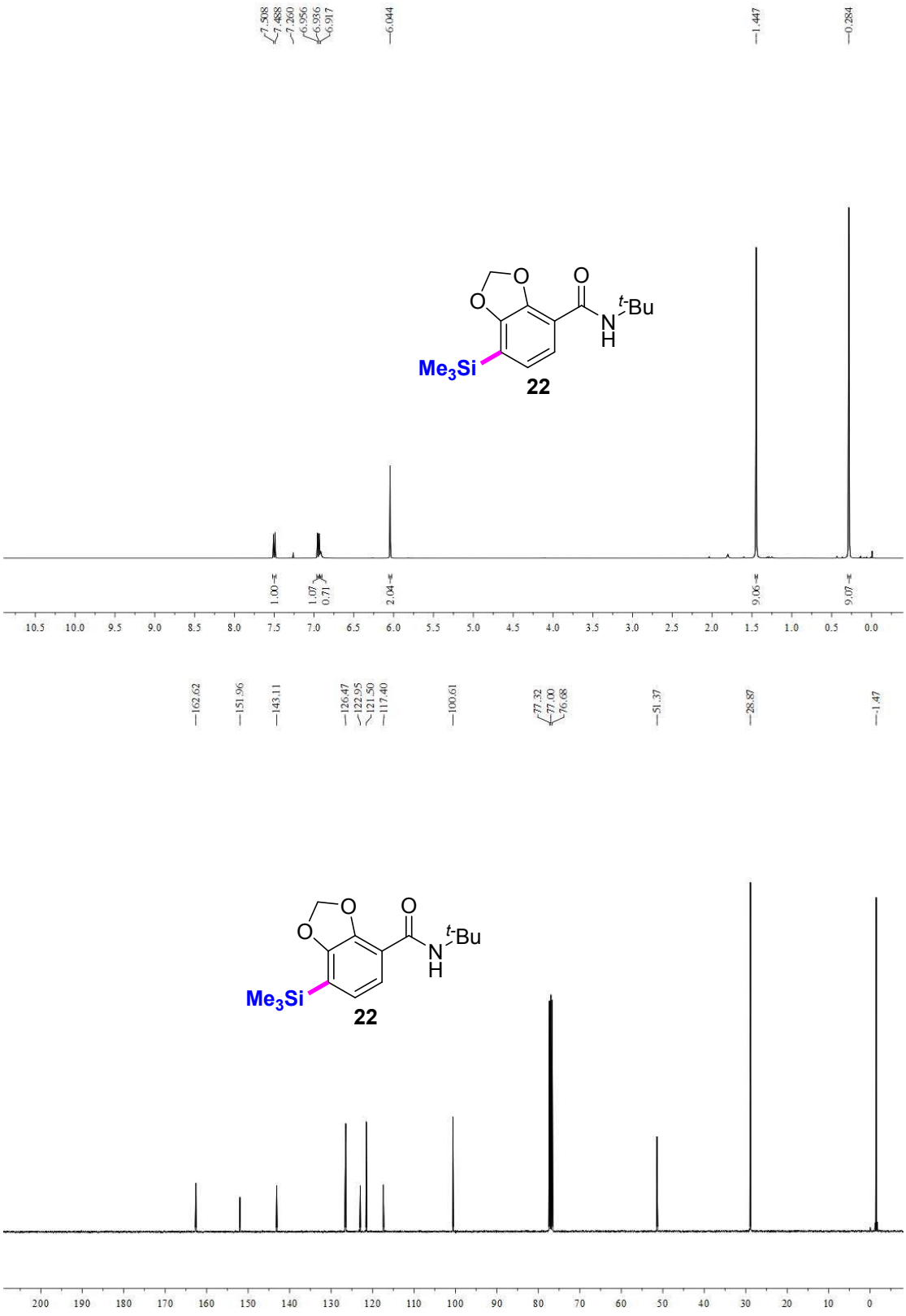
^{19}F NMR spectra in $CDCl_3$ for compound 19



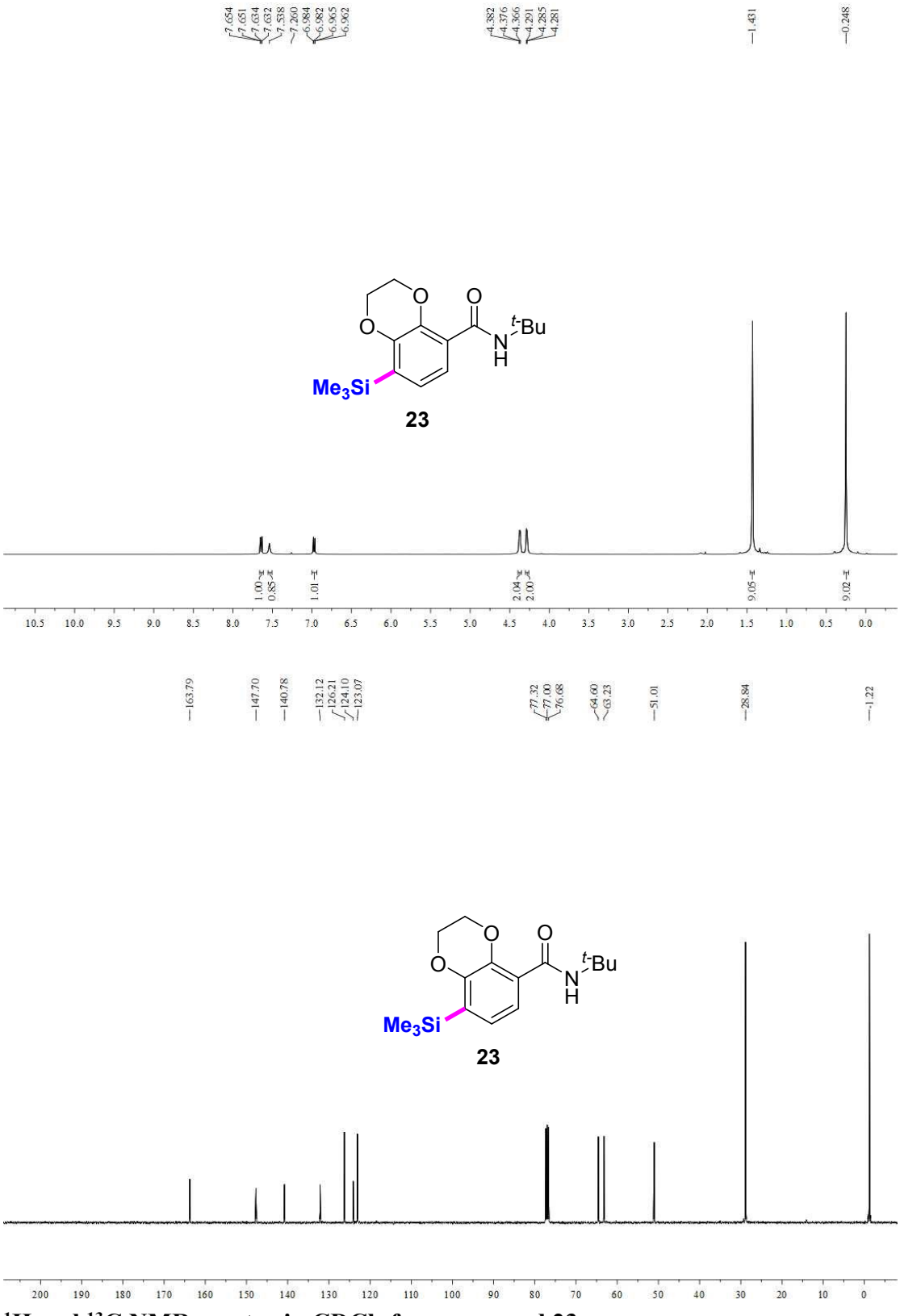
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 20



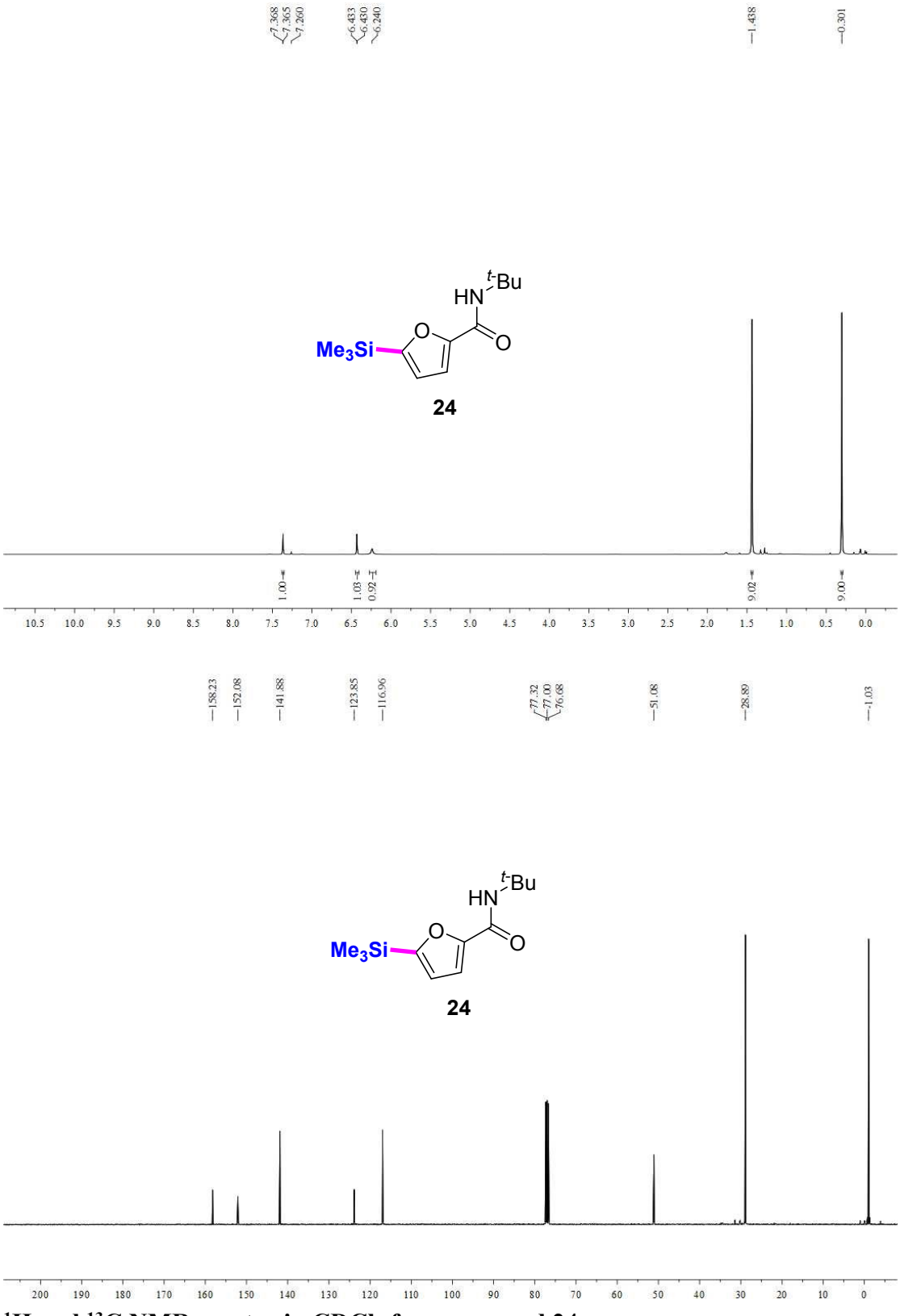
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 21



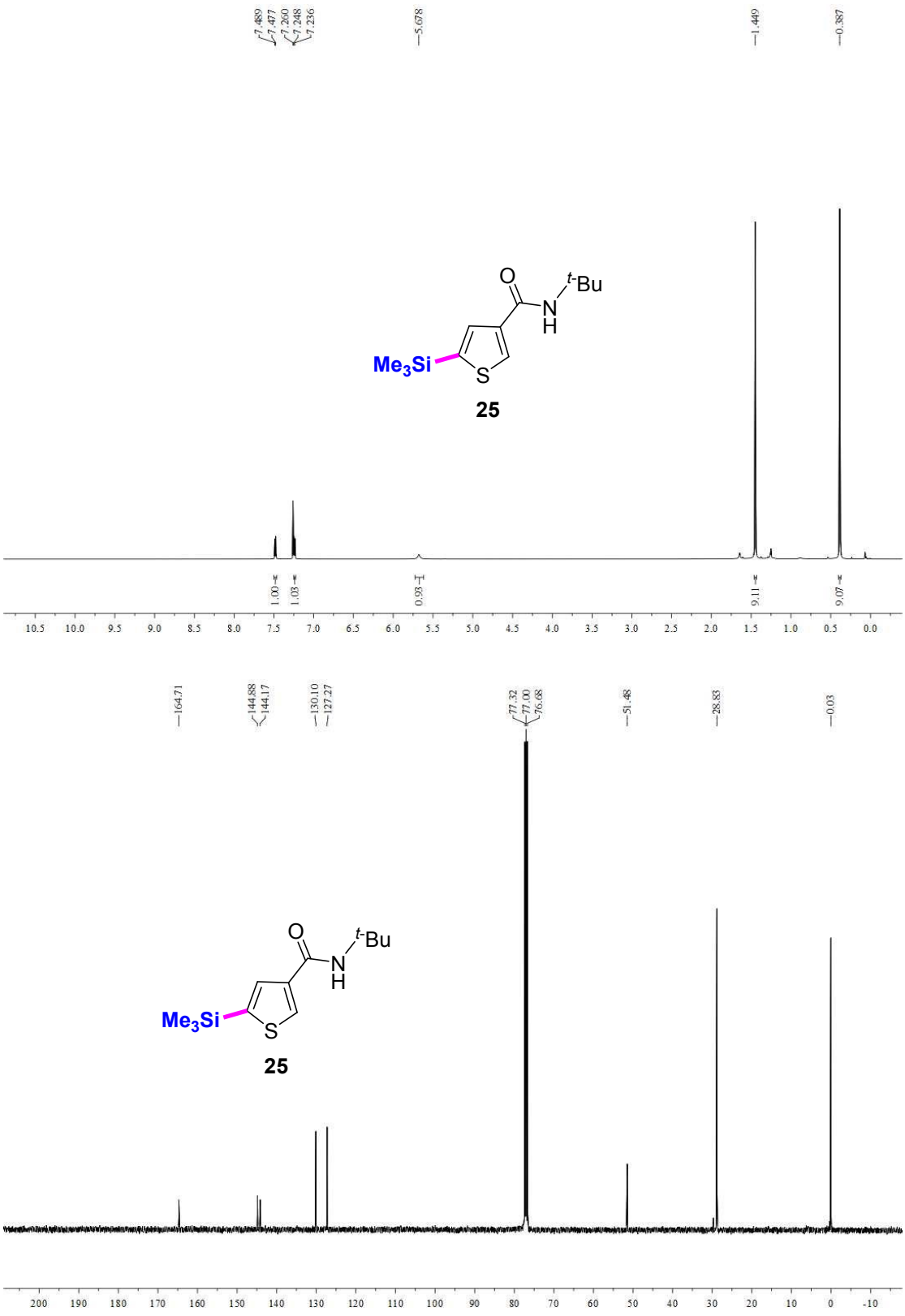
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 22



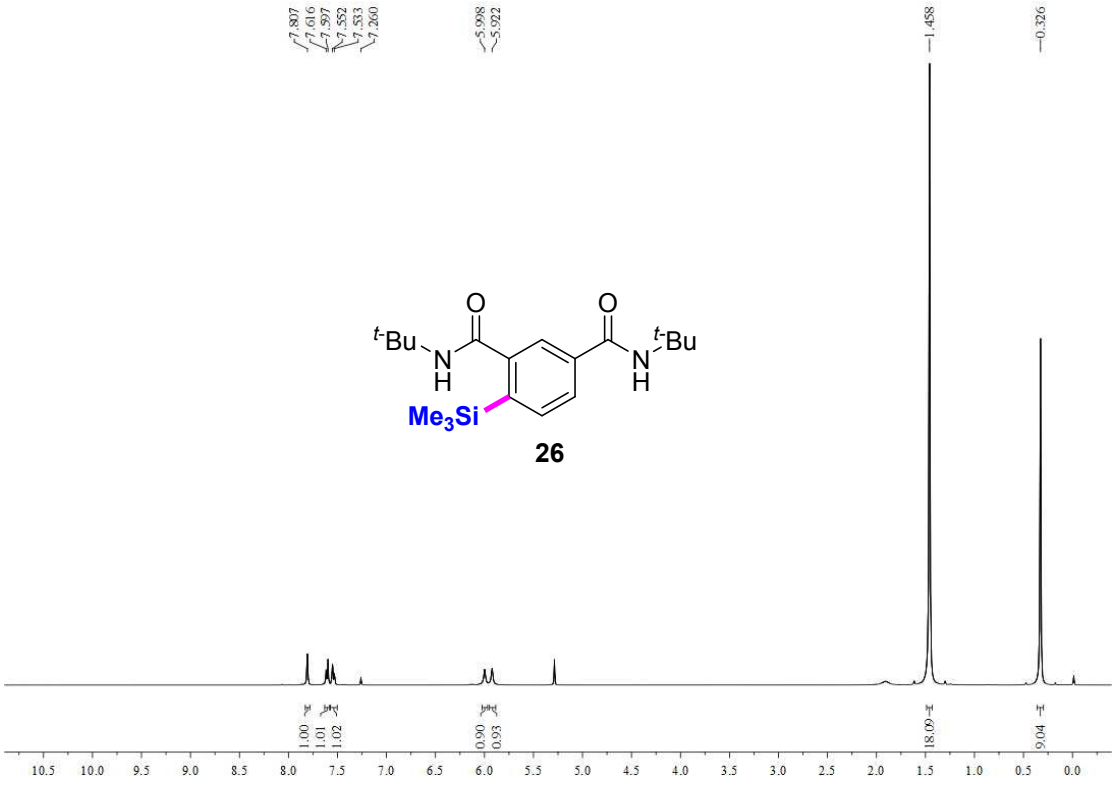
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 23

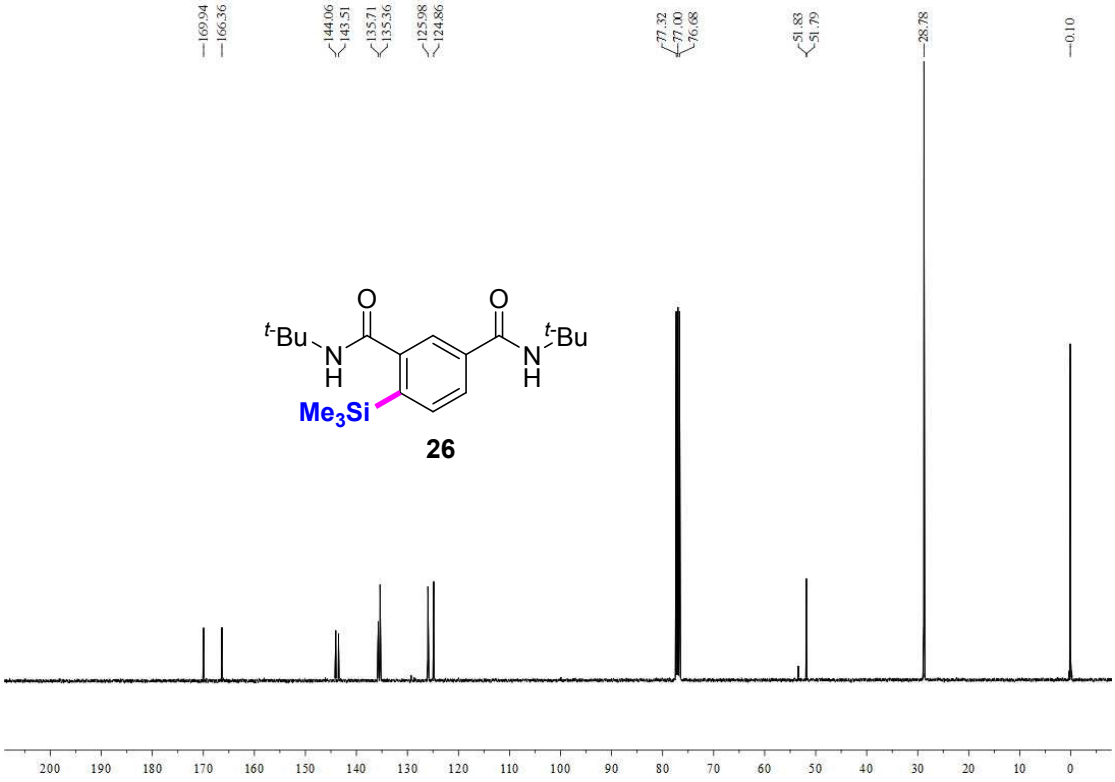


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 24

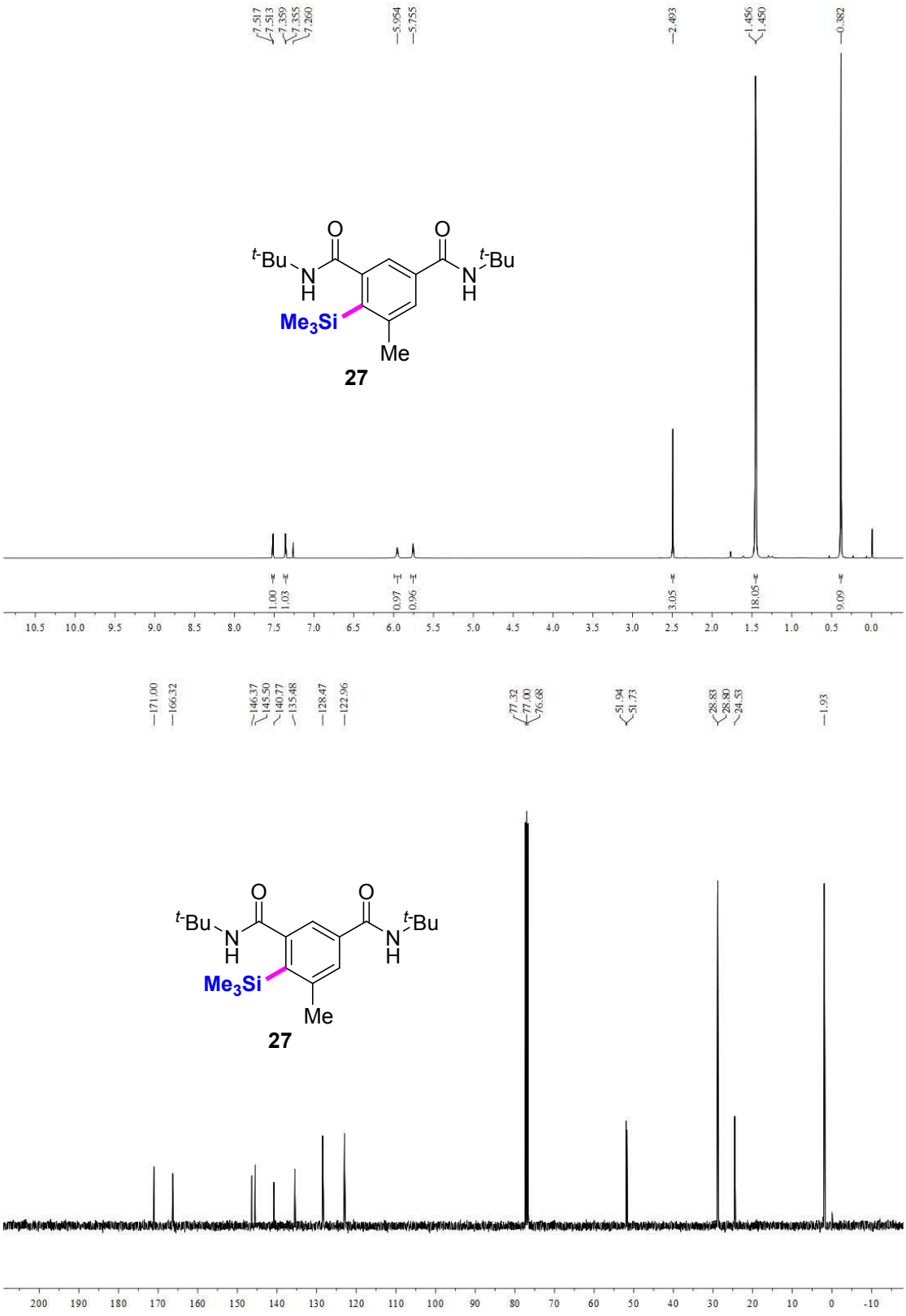


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 25

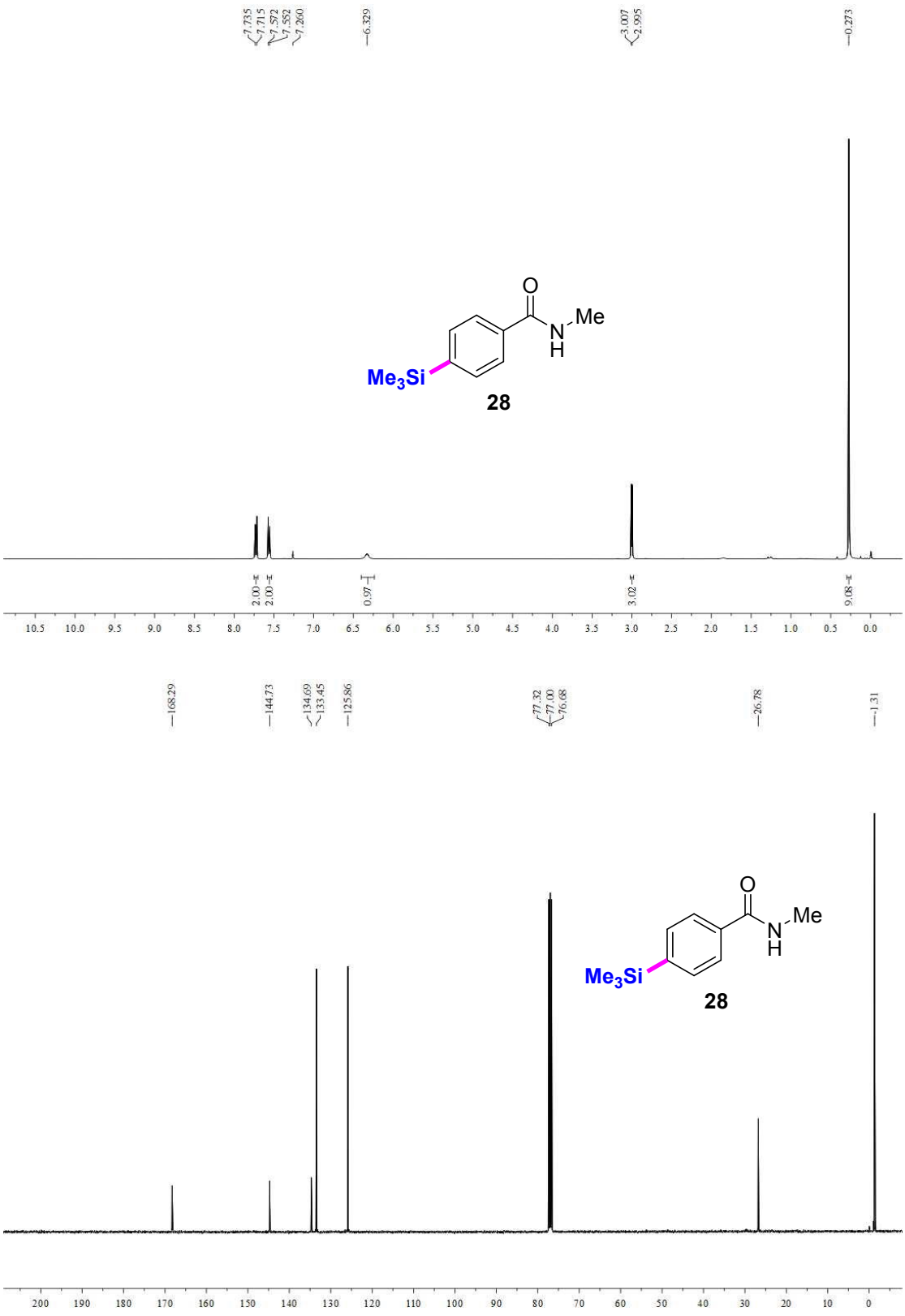




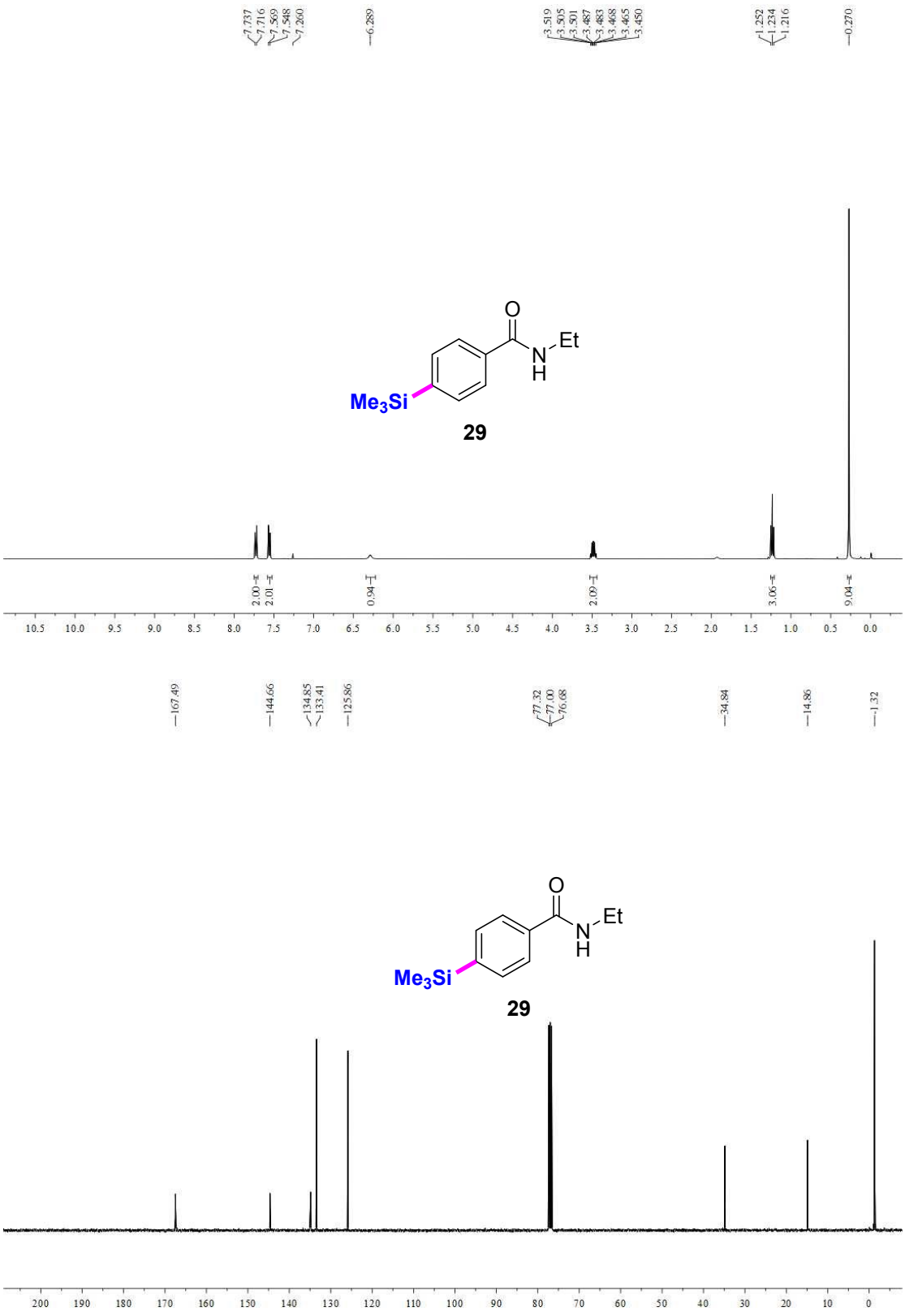
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 26



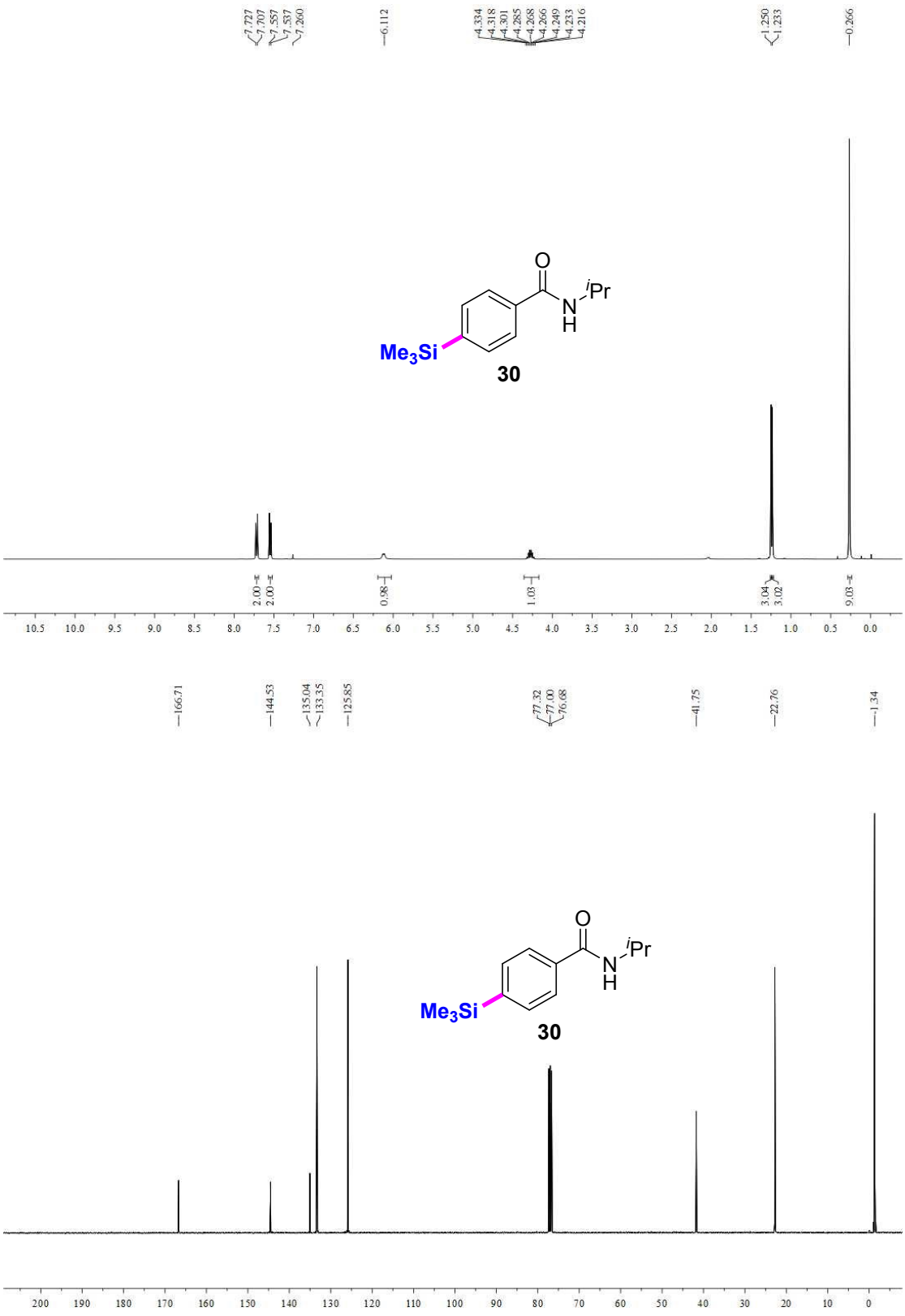
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 27



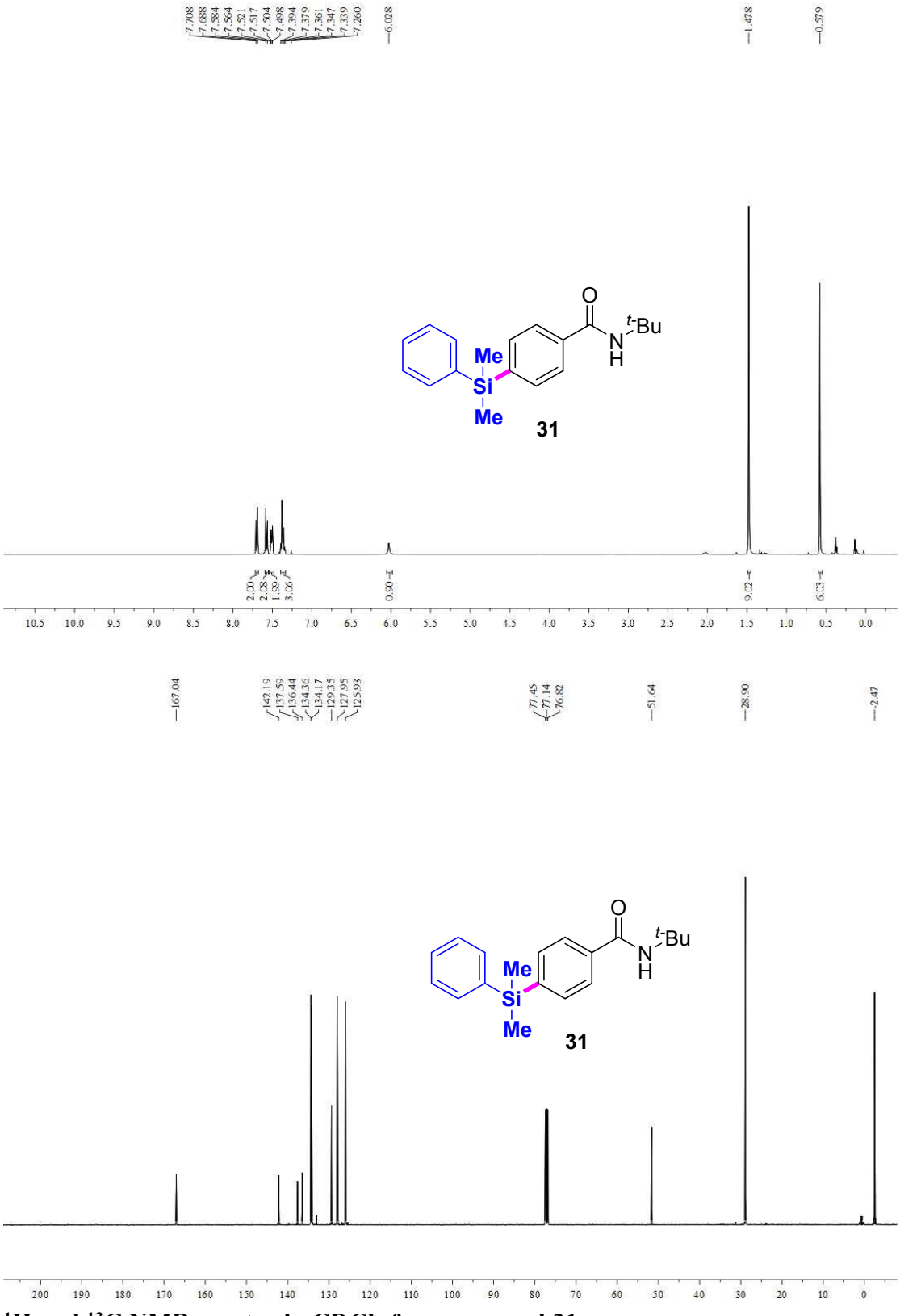
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 28



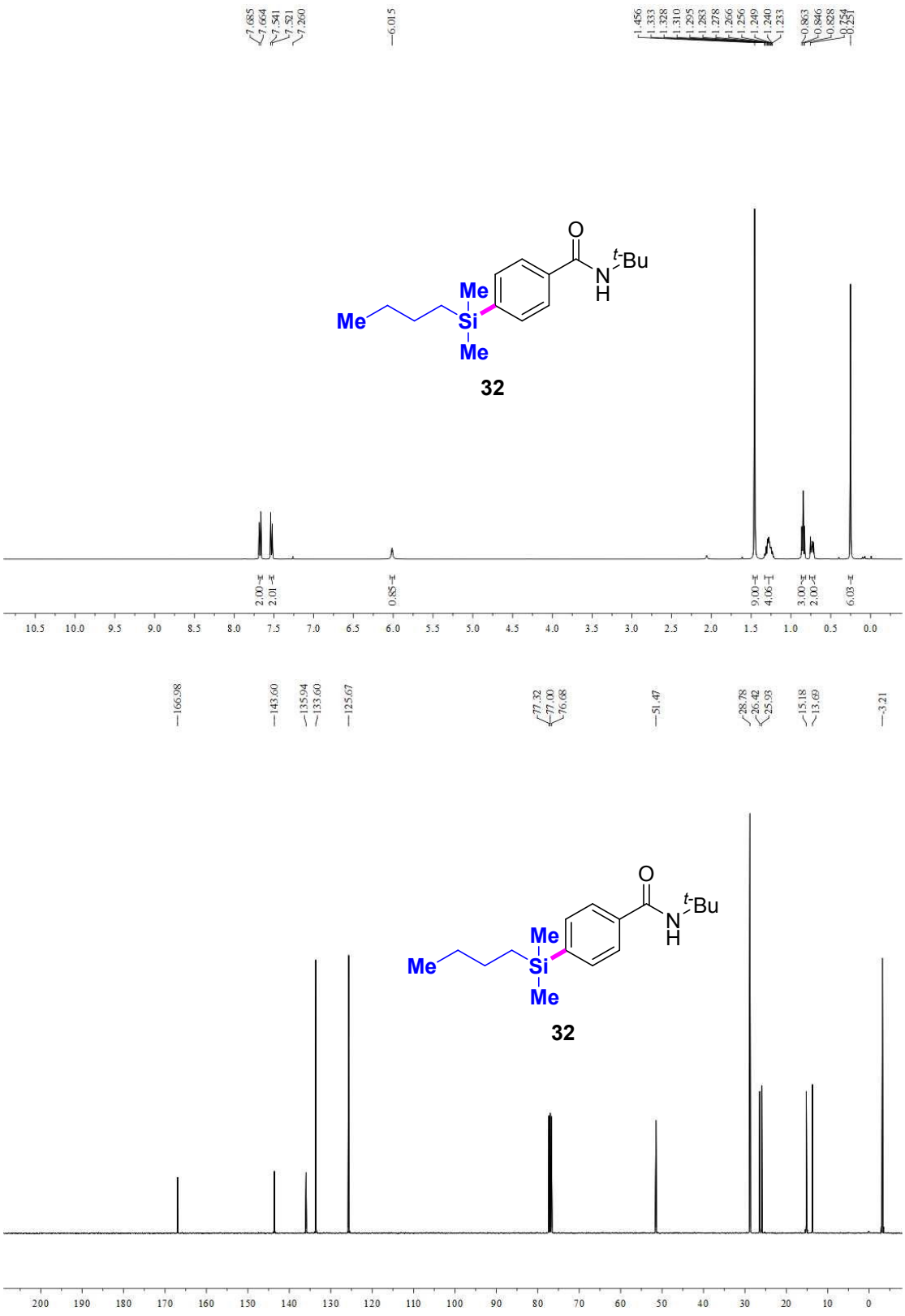
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 29



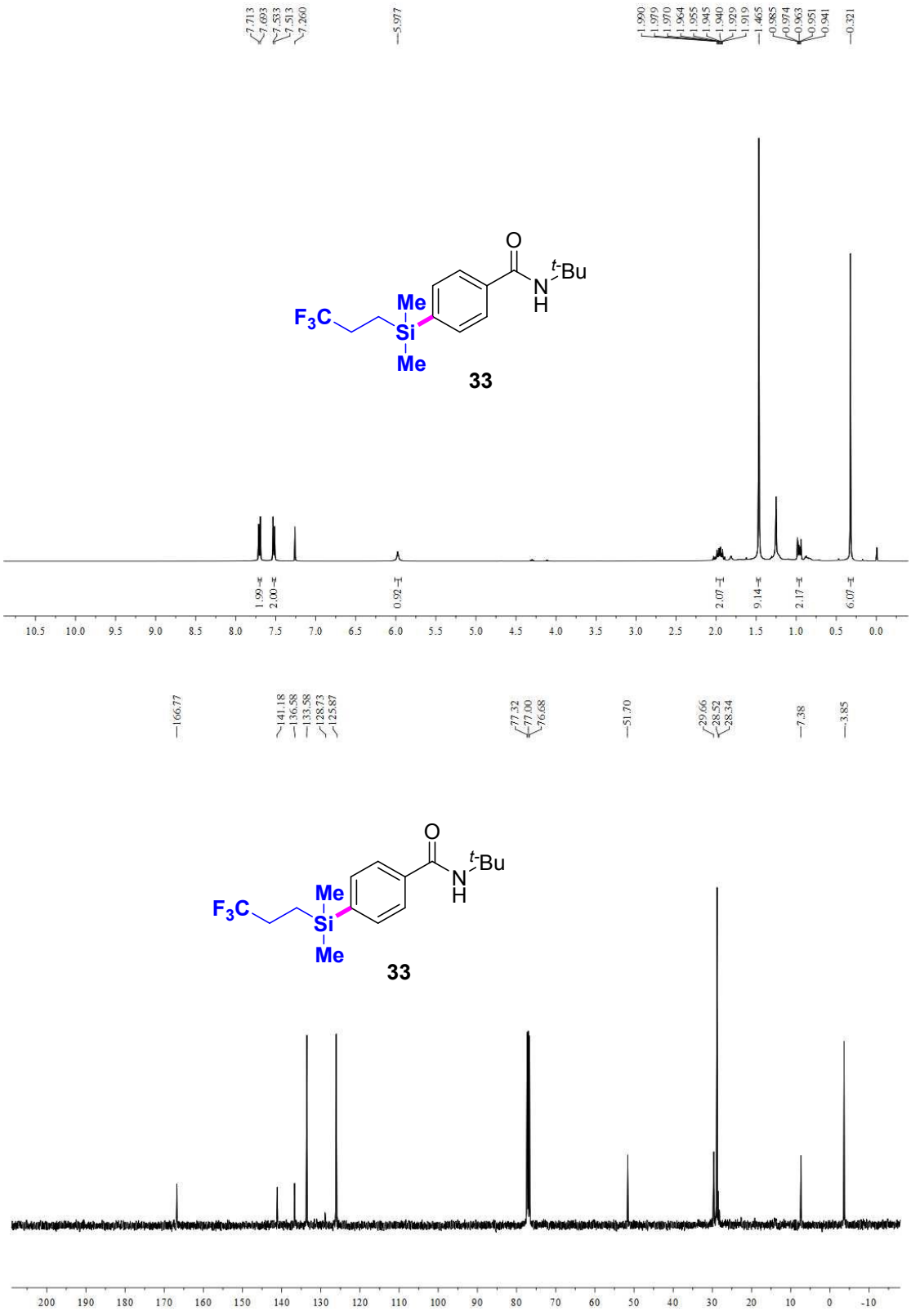
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 30



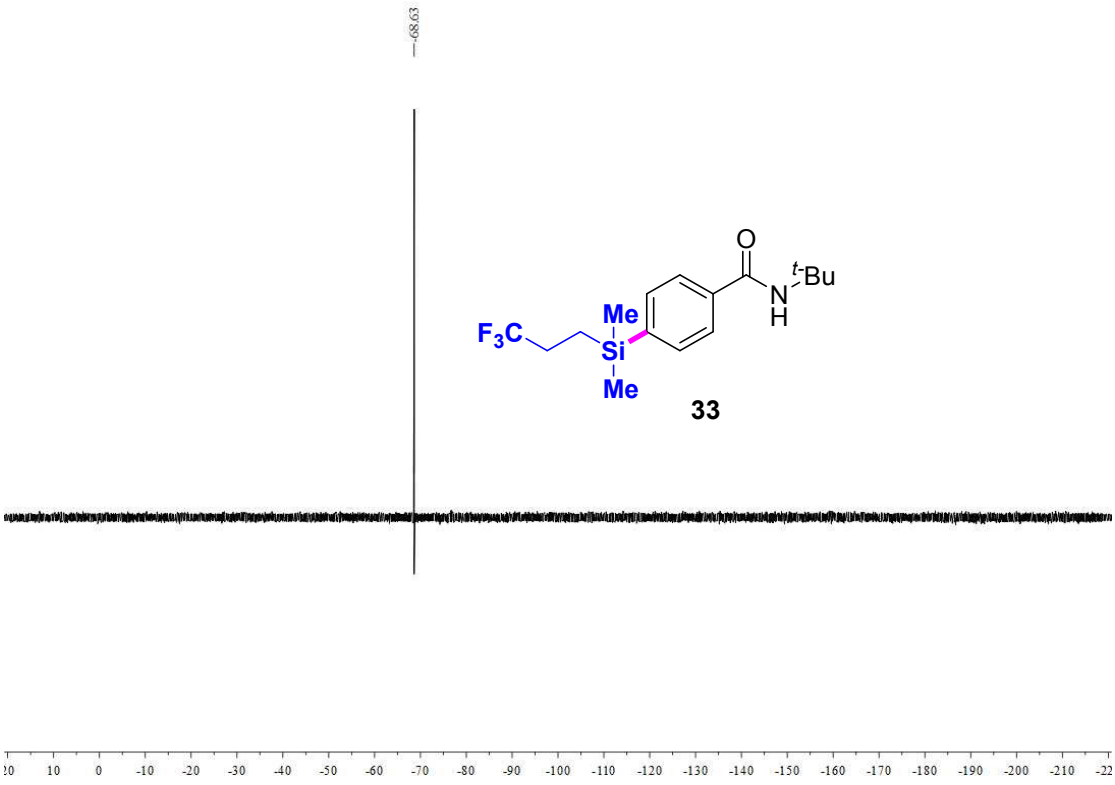
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 31



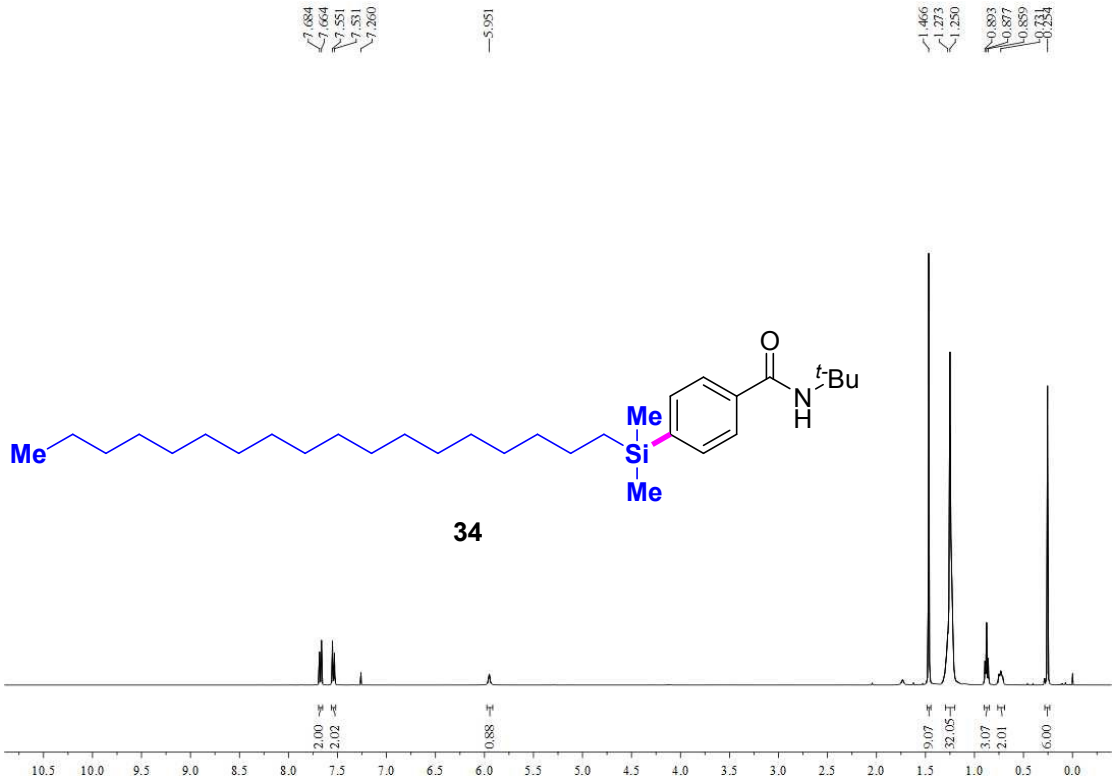
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 32

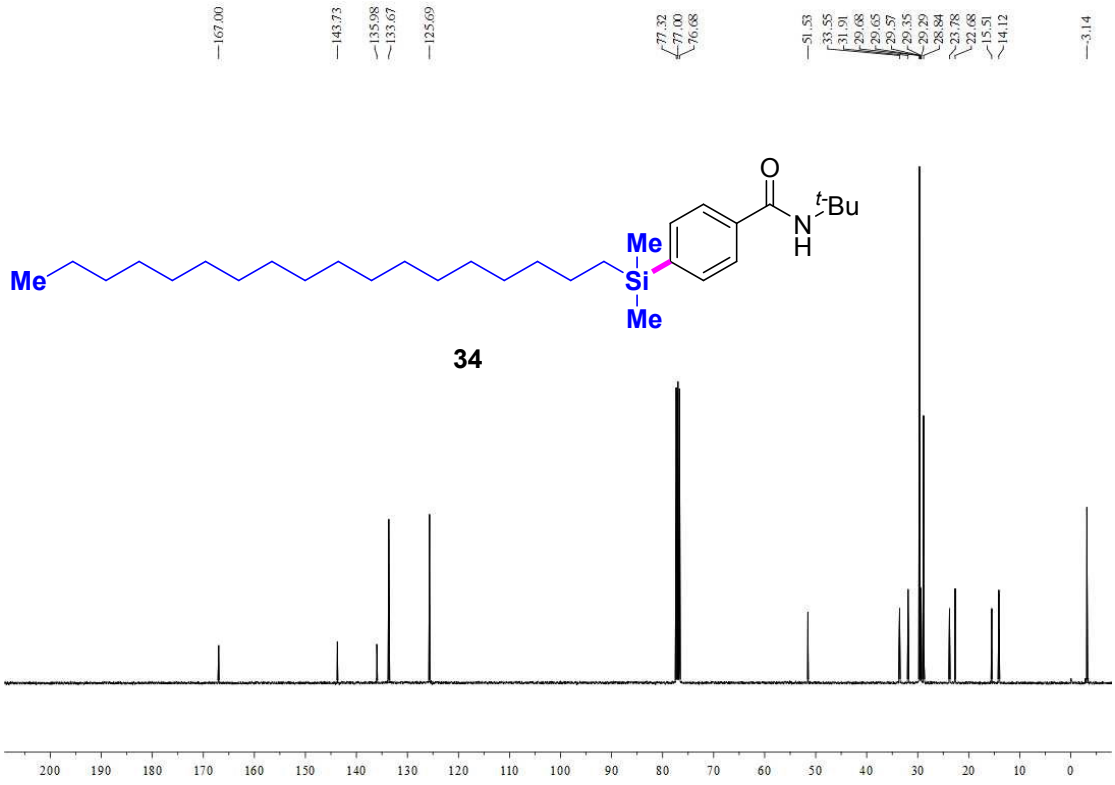


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 33

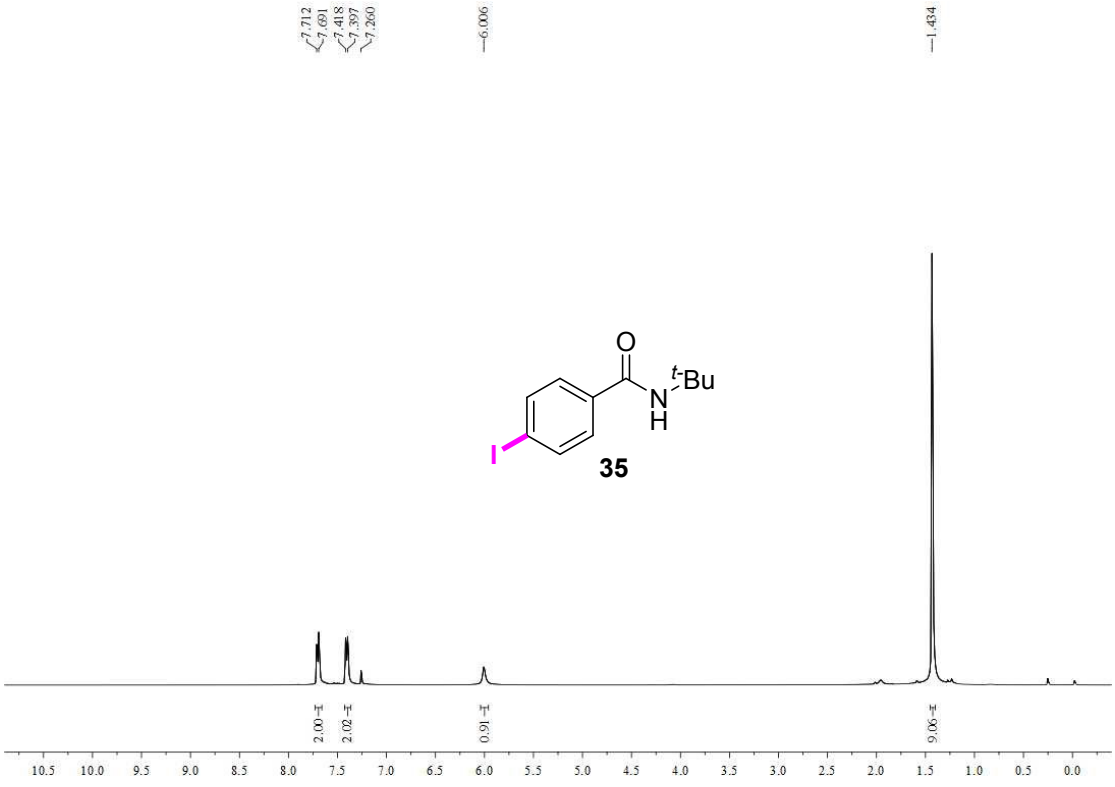


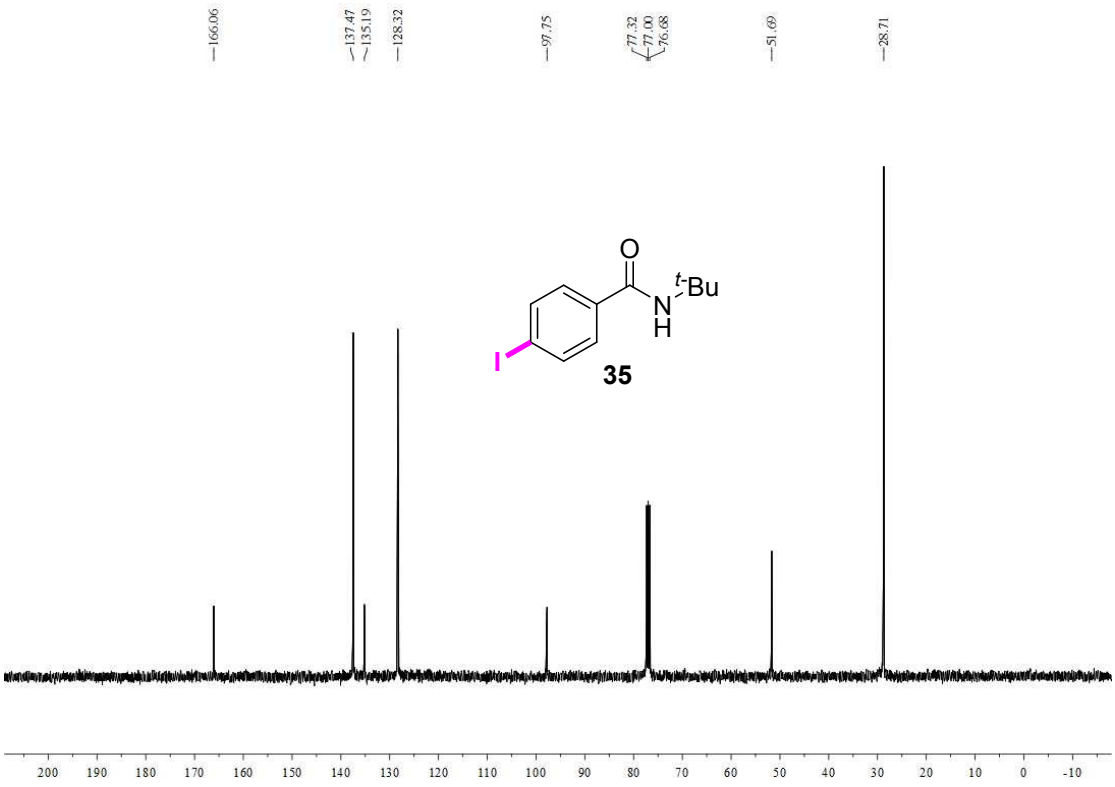
^{19}F NMR spectra in $CDCl_3$ for compound 33



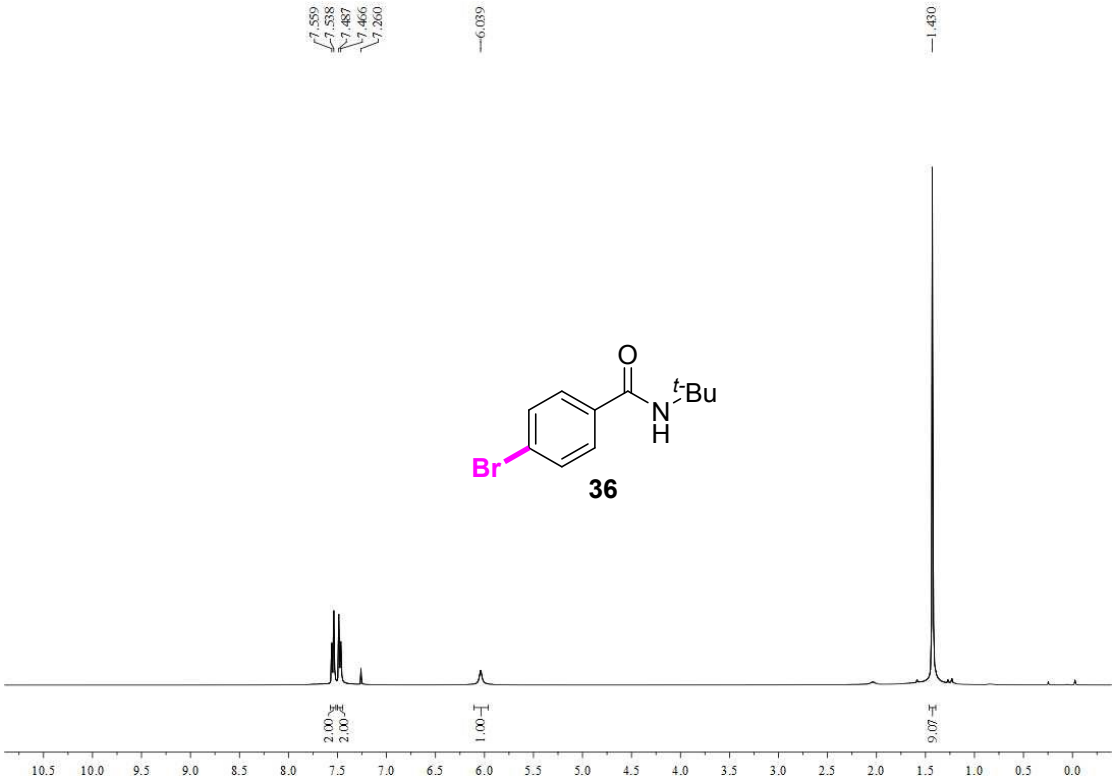


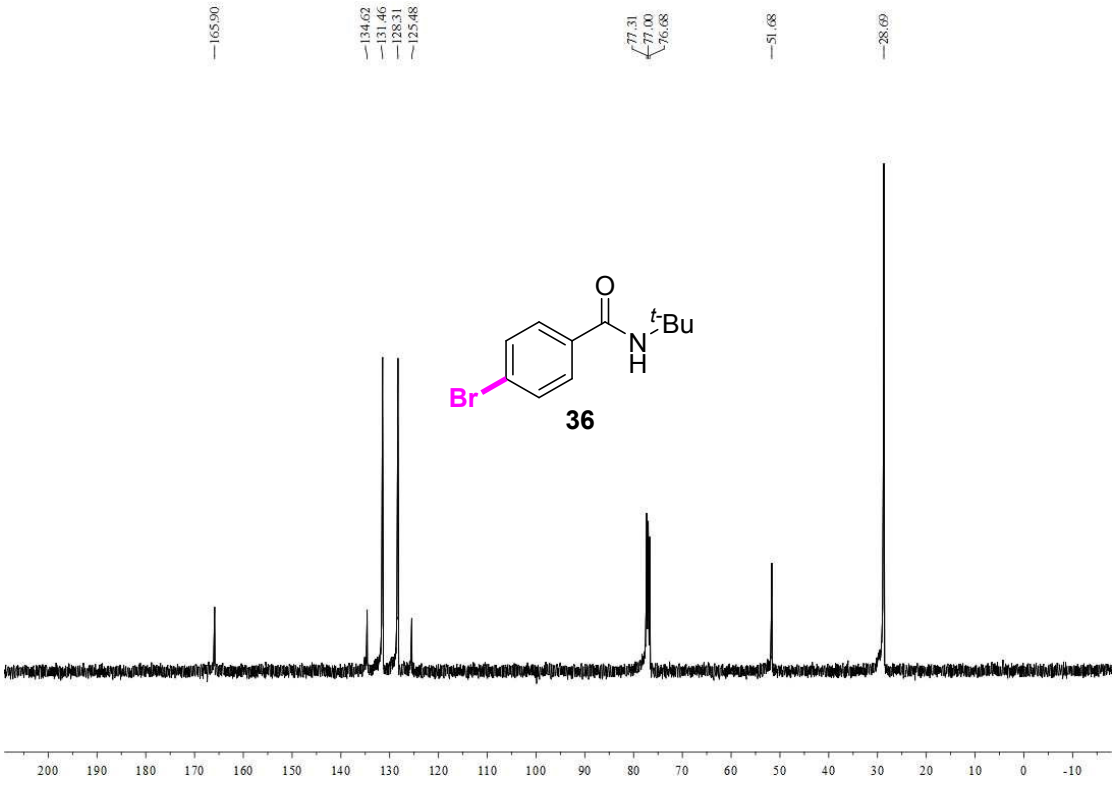
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 34



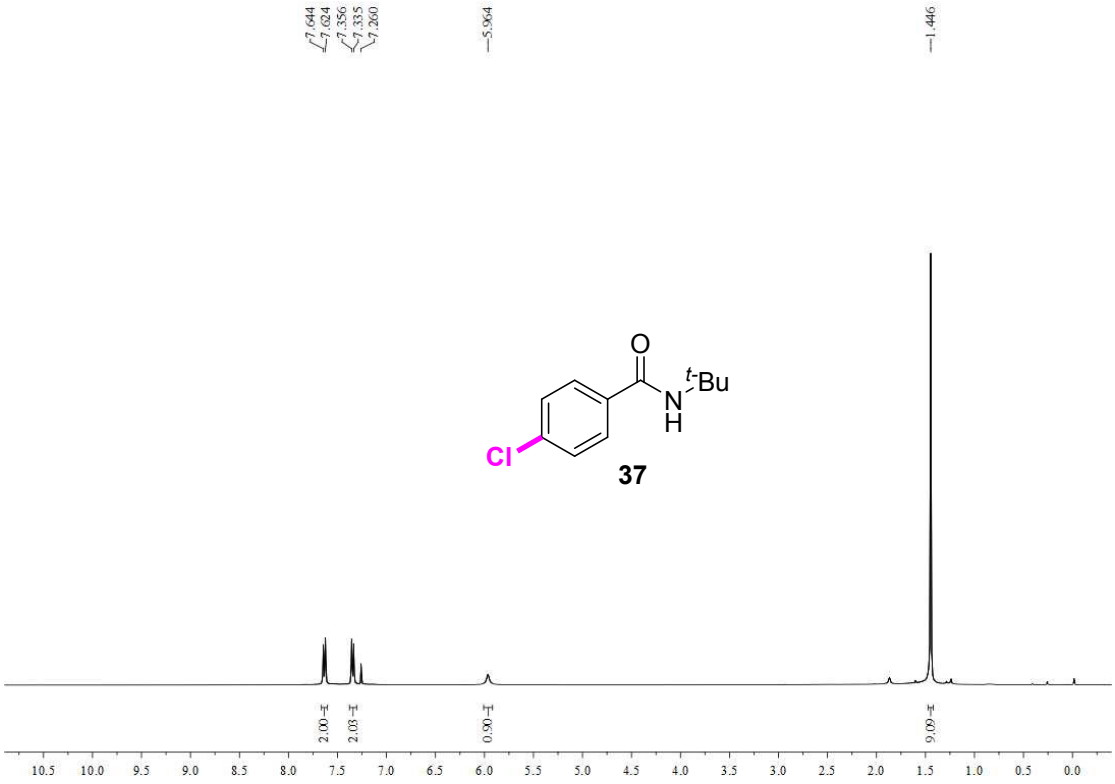


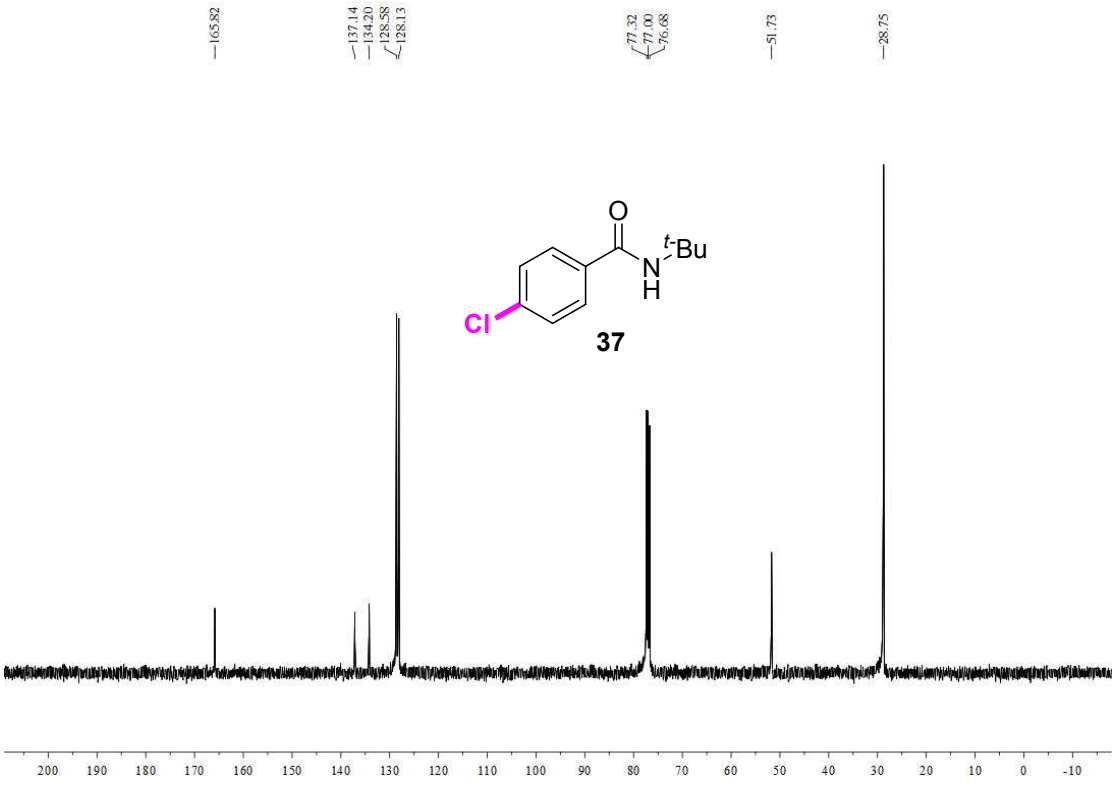
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 35



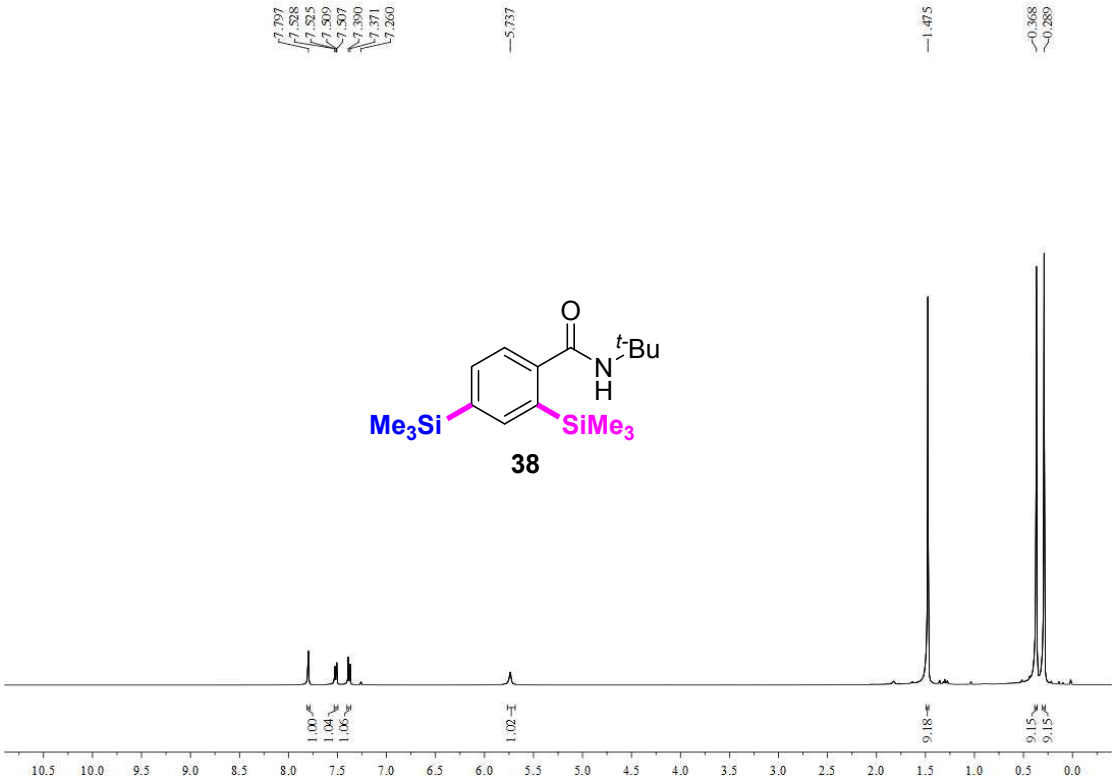


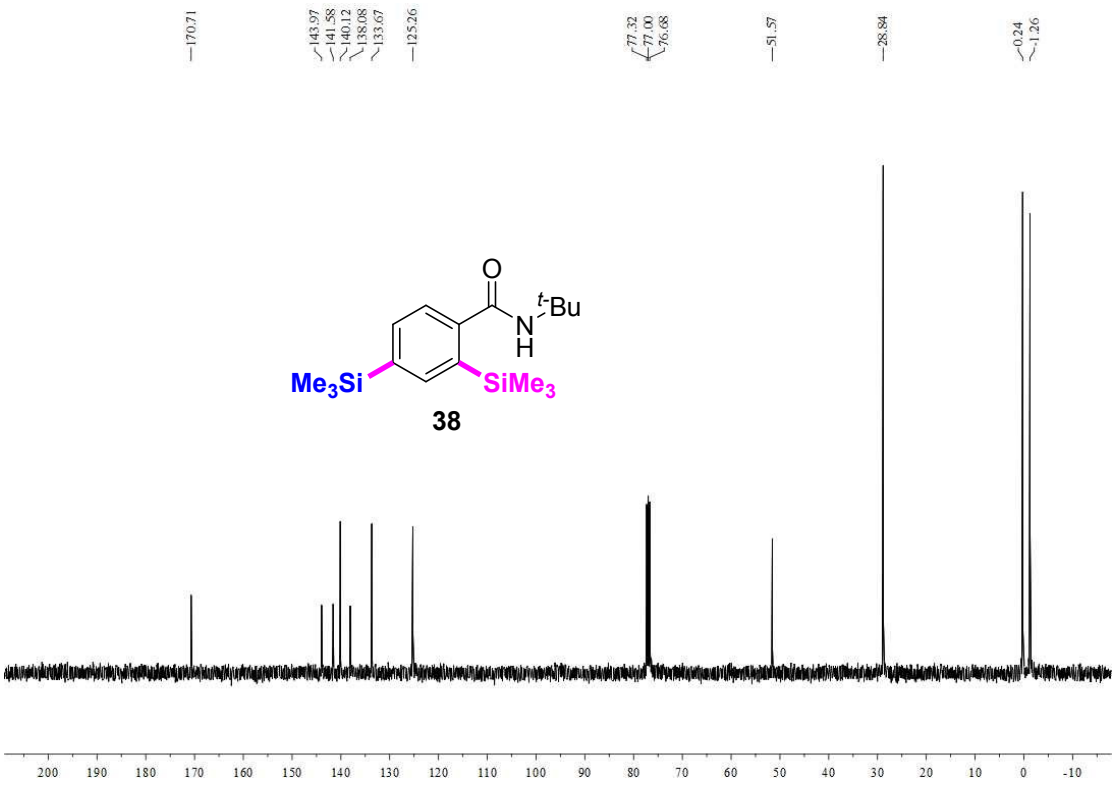
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 36



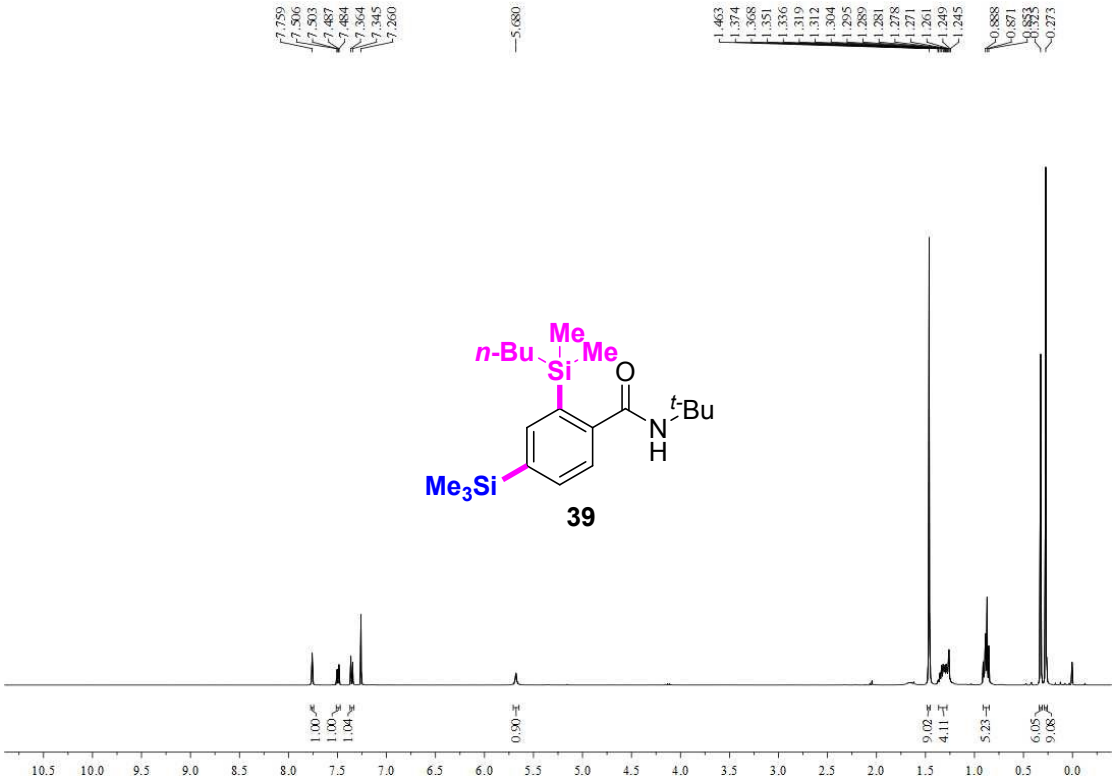


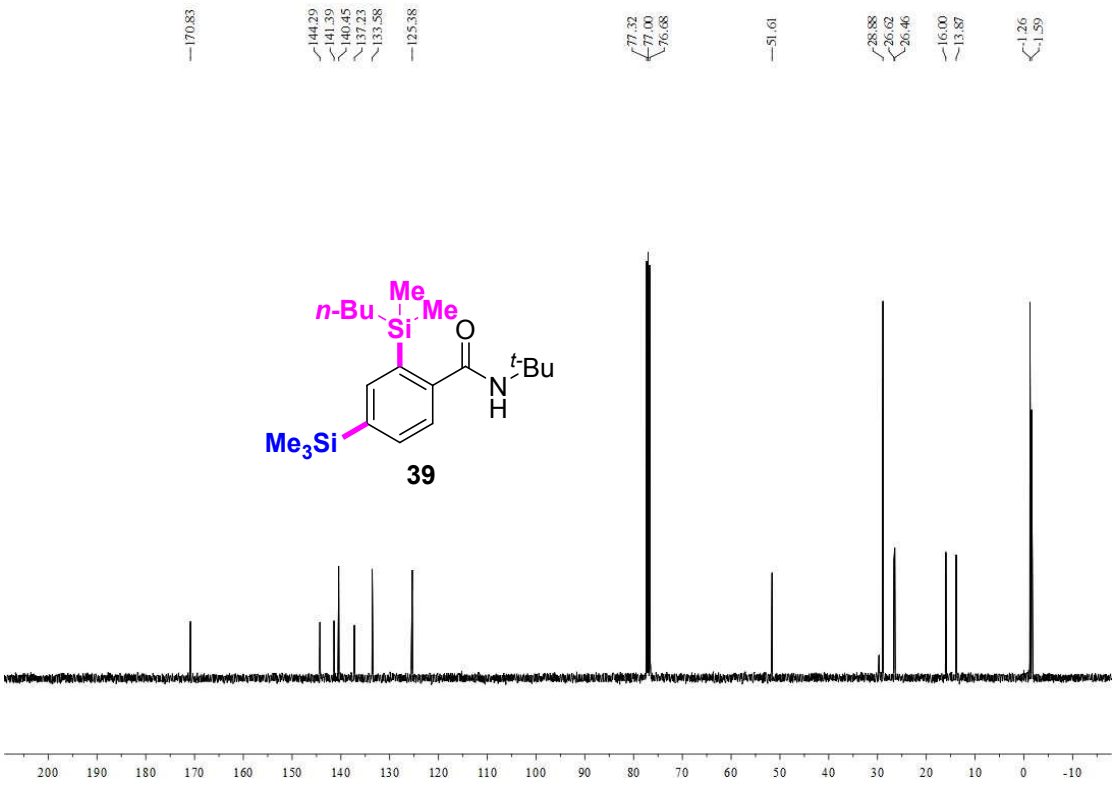
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 37



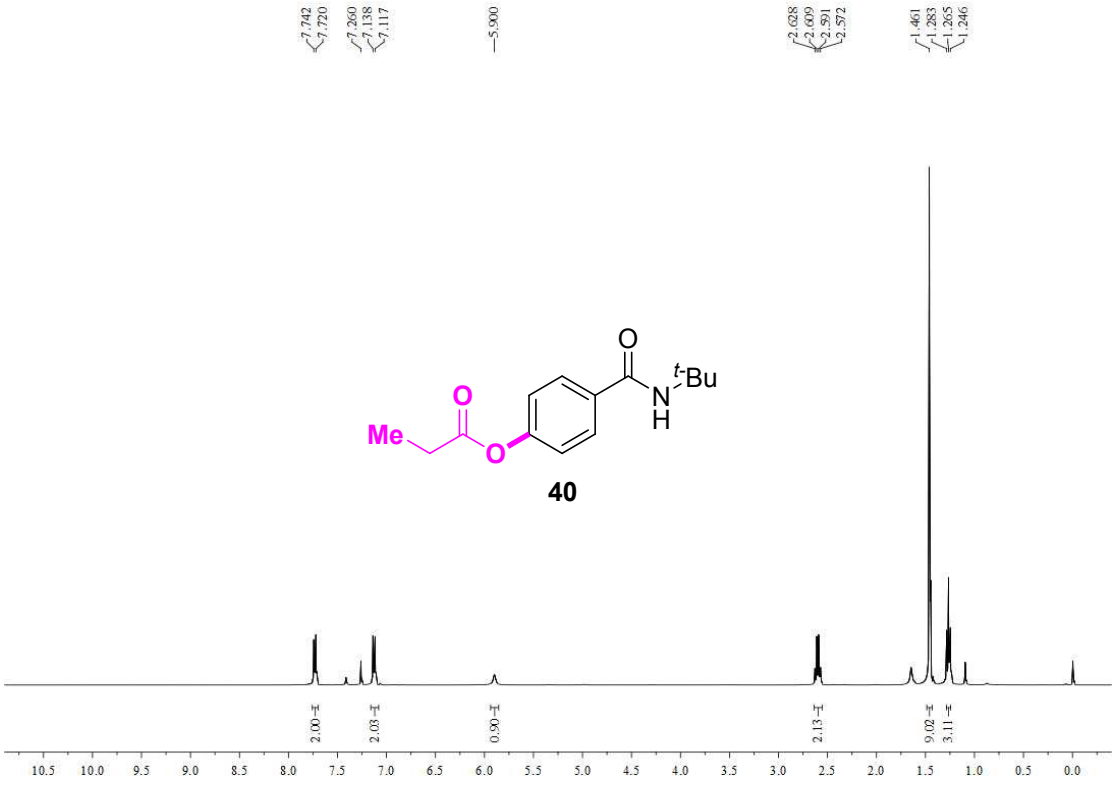


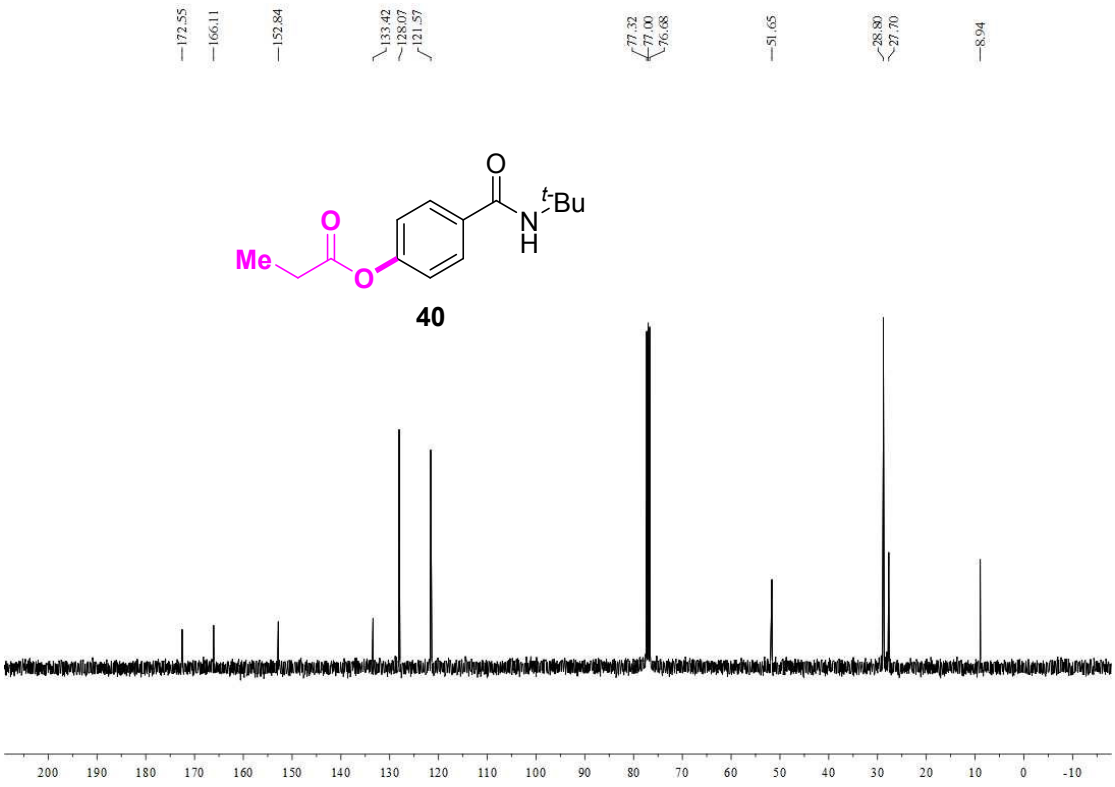
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 38



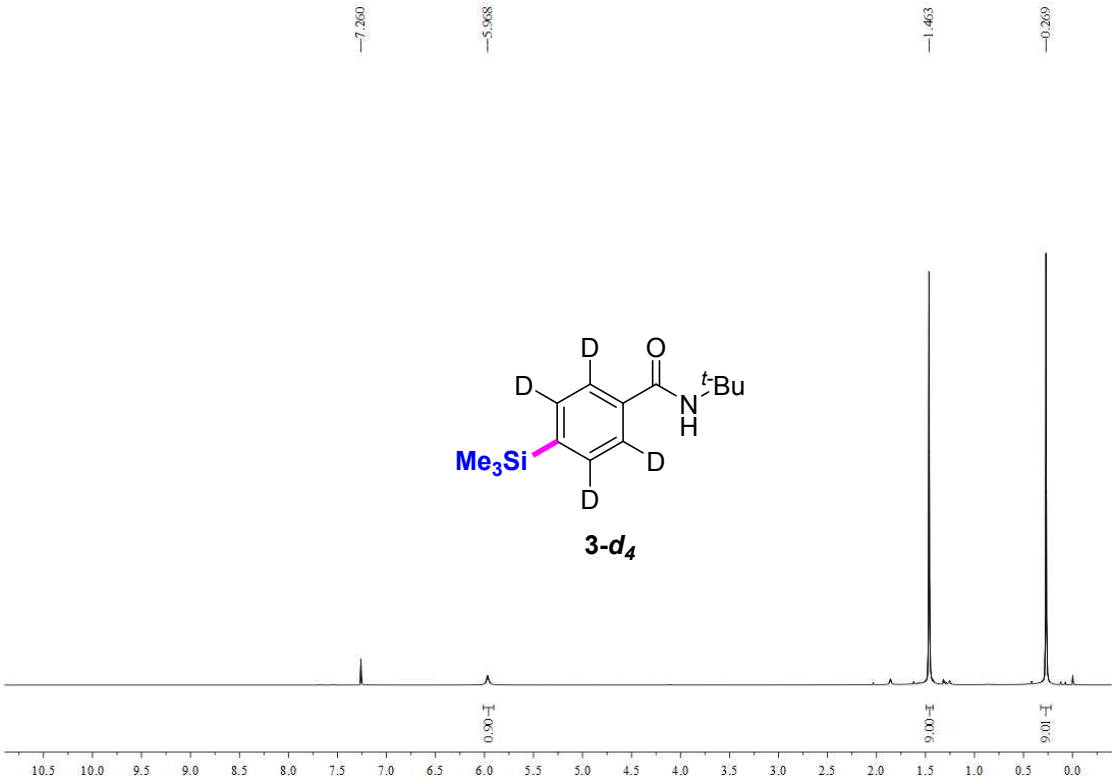


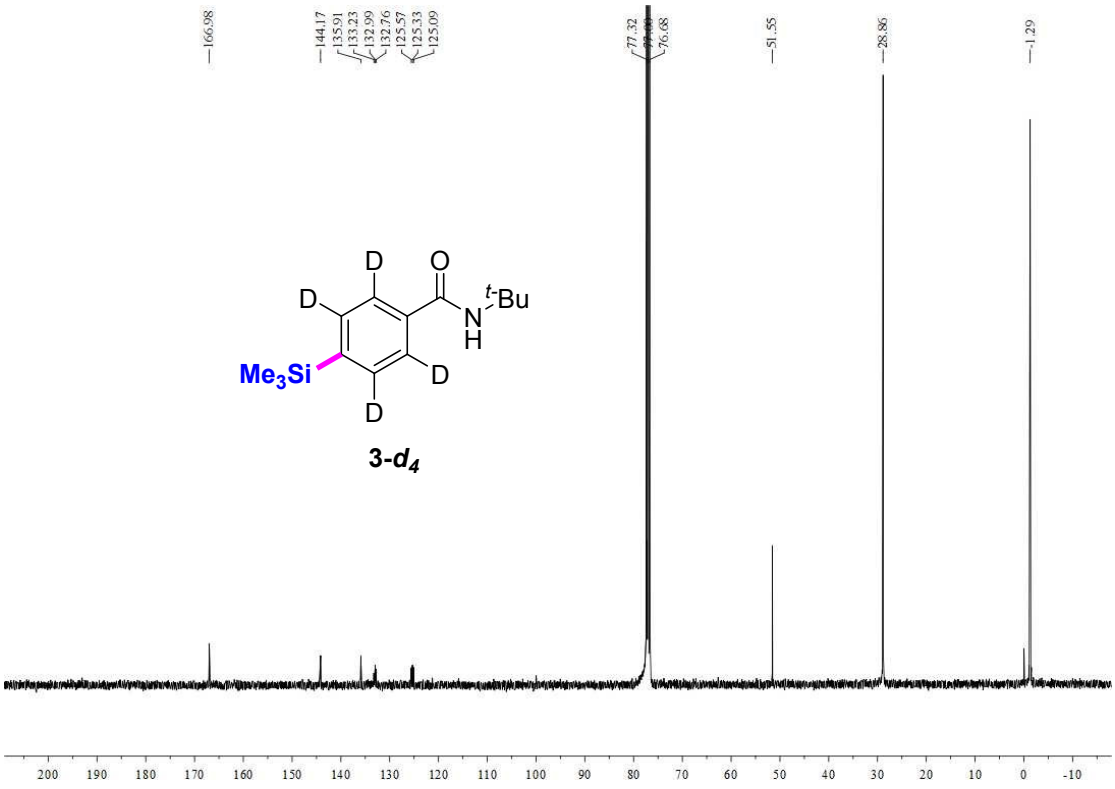
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 39





^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 40





^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3-*d*$_4$