*Supporting Information*

# Synthesis of Acyl Fluorides *via* DAST-Mediated Fluorinative C–C Bond Cleavage of Activated Ketones

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## 1. Materials and Methods

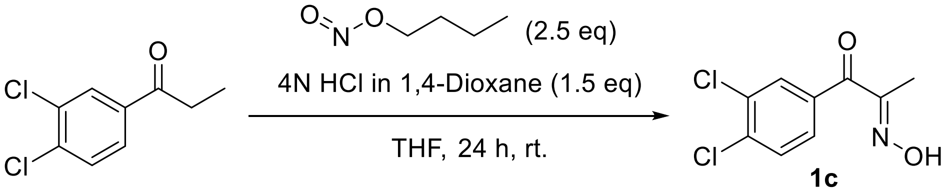
Dichloromethane ($CH_2Cl_2$), tetrahydrofuran (THF), and acetonitrile ($CH_3CN$) were directly used from SPS system (Hansen, Puresolve MD) without further purification. Thin layer chromatography (TLC) analysis was run on silica gel plates. Spots were visualized by exposure to ultraviolet (UV) light (254 nm) or by staining with $KMnO_4$ aq. solution and then heating. High Resolution Mass Spectrometric analysis were performed on JEOL JMS-700 [Ionization mode: EI and FAB; Mass analyzer type: Double-focusing type (magnetic sector-electrostatic sector)]. High-resolution mass spectra were reported for the molecular ion $[M]^+$, $[M+H]^+$. Nuclear magnetic resonance (NMR) spectra were recorded either on Ascend 400, Bruker 300 or 500 UltraShield (either on 300, 400, 500 MHz for $^1H$, 376 MHz for $^{19}F$ NMR, and either on 100 or 125 MHz for $^{13}C$). The fluorine spectra are unreferenced. Chemical shifts for proton NMR spectra are reported in parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d*, to the quintet at 3.31 ppm for methanol-*d*, and to the quintet at 2.50 ppm for dimethylsulfoxide-$d_6$. Chemical shifts for carbon NMR spectra are reported in 77.2 ppm with the center line of triplet for chloroform-*d*, in 49.1 ppm with the center line of the septet for methanol-*d* and in 39.5 ppm with the center line of the septet for dimethylsulfoxide-$d_6$. Data for $^1H$ NMR were presented as following: chemical shifts (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. The chemical shifts of peaks found were reported for $^{13}C$ NMR spectra. Infrared spectra were recorded with a Smith Detection ATR-FTIR instrument.

## 2. Experimental Procedures and Characterization Data

### Preparation of α-oximinoketones (compounds 1 and 3)

The known starting materials **1a**,[1] **1b**,[2] **1d**,[2] **3a**,[3] **3d**,[3] **3f**,[4] **3g**,[5] **3h**,[6] **3i**,[7] **3l**,[8] **3p**,[9] and **3s**[10] were not characterized.

1) Procedure for acid-assisted oximation



To a stirred solution of ketone (606 mg, 3.0 mmol), n-butyl nitrite (0.88 mL, 7.5 mmol) in THF (9.0

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[1] Gutierrez, R. U.; Rebollar, A.; Bautista, R.; Pelayo, V.; Vargas, J.; Montenegro, M. M.; Espinoza-Hicks, C.; Ayala, F.; Bernal, P. M.; Carrasco, C.; Zepeda, L. G.; Delgado, F.; Tamariz, J. *Tetrahedron: Asymmetry* **2015**, *26*, 230.

[2] Reddy, M. K.; Mallik, S.; Ramakrishna, I.; Baidya, M. *Org. Lett.* **2017**, *19*, 1694.

[3] Schlegel, M.; Schneider, C. *Org. Lett.* **2018**, *20*, 3119.

[4] Katritzky, A. R.; Wang, Z.; Hall, C. D.; Akhmedov, N.; Shestopalov, A. A.; Steel, P. J. *J. Org. Chem.* **2003**, *68*, 9093.

[5] Cotman, A. E.; Lozinsek, M.; Wang, B.; Stephan, M.; Mohar, B. *Org. Lett.* **2019**, *21*, 3644.

[6] Chow, Y. L.; Wu, Z. Z. *J. Am. Chem. Soc.* **1987**, *109*, 5260.

[7] Shukla, S.; Srivastava, R. S.; Shrivastava, S. K.; Sodhi, A.; Kumar, P. *Appl. Biochem.* **2012**, *167*, 1430.

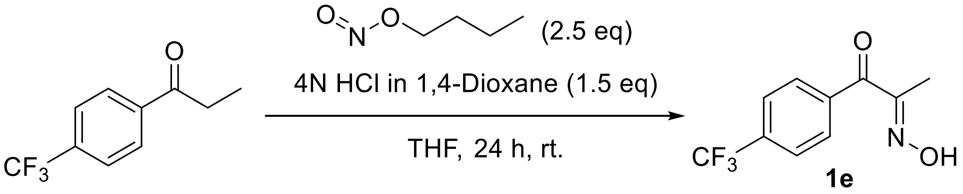
[8] Baidya, M. Yamamoto, H. *J. Am. Chem. Soc.* **2011**, *133*, 13880.

[9] Bosiak, M.; Pakulski, M. M. *Synthesis* **2011**, 316.

[10] Berenyi, A.; Minorics, R.; Ivanyi, Z.; Ocsovszki, I.; Ducza, E.; Thole, H.; Messinger, J.; Wolfling, J.; Motyan, G.; Mernyak, E.; Frank, E.; Schneider, G.; Zupko, I. *Steroids* **2013**, 78, 69.

mL) was added 4N HCl in 1,4-dioxane (1.1 mL, 4.5 mmol). After 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1c** (547 mg, 79%) as a white solid.

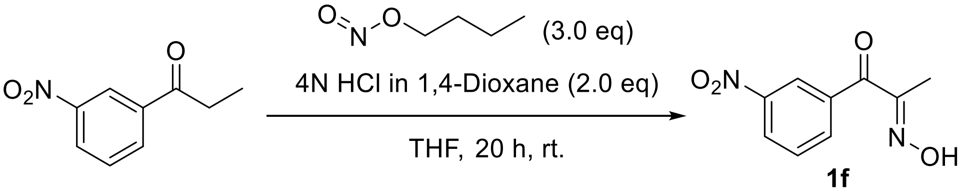
**(E)-1-(3,4-dichlorophenyl)-2-(hydroxyimino)propan-1-one (1c);** $R_f$ = 0.5 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 8.03 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.1 and 1.9 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 2.17 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.1, 157.1, 137.4, 136.0, 132.7, 132.6, 130.3, 129.6, 10.0. IR (neat) $\nu_{max}$ 3255, 1639, 1442, 1331, 1020 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_7Cl_2NO_2$ [M]$^+$ 230.9854, found 230.9864.



1e

To a stirred solution of ketone (606 mg, 3.0 mmol), n-butyl nitrite (0.88 mL, 7.5 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.1 mL, 4.5 mmol). After 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1e** (499 mg, 72%) as a white solid.

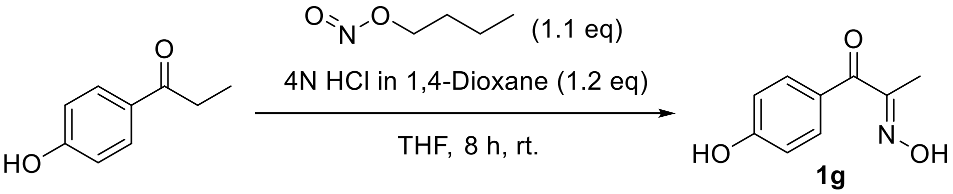
**(E)-2-(hydroxyimino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (1e)**; $R_f$ = 0.4 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.8, 157.3, 139.6, 133.8 (q, $J_{C,F}$ = 33 Hz), 130.7, 125.1 (q, $J_{C,F}$ = 4 Hz), 122.4, 9.9. IR (neat) $\nu_{max}$ 3246, 1662, 1312, 1108, 1003 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_8F_3NO_2$ [M]$^+$ 231.0507 found 231.0506.



1f

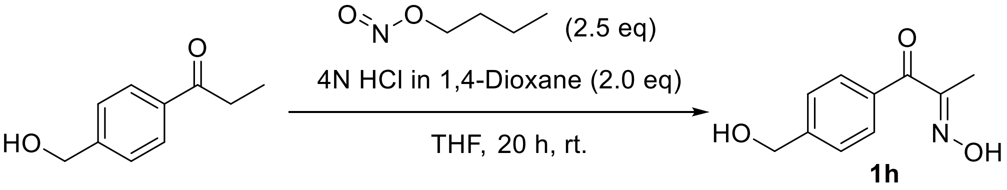
To a stirred solution of ketone (537 mg, 3.0 mmol), n-butyl nitrite (1.05 mL, 9.0 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 20 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1f** (462 mg, 74%) as a white solid.

**(E)-2-(hydroxyimino)-1-(3-nitrophenyl)propan-1-one (1f);** $R_f$ = 0.5 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.81 (br s, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 8.09 (s, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.1, 157.1, 147.9, 137.8, 136.0, 129.3, 126.9, 125.9, 9.8. IR (neat) $\nu_{max}$ 3177, 2864, 1610, 1526, 1016 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_8N_2O_4$ [M]$^+$ 208.0484, found 208.0480.



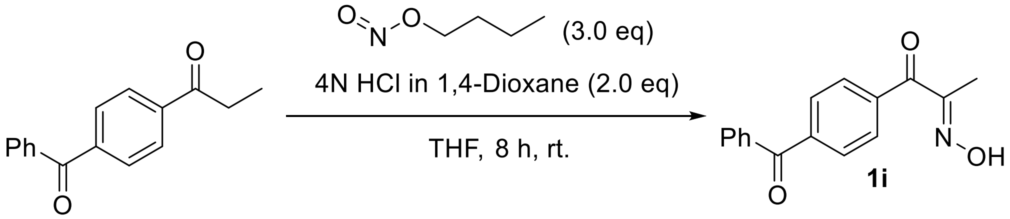
To a stirred solution of ketone (450 mg, 3.0 mmol), n-butyl nitrite (0.38 mL, 3.3 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (0.9 mL, 3.6 mmol). After 8 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1g** (279 mg, 52%) as a white solid.

**(E)-2-(hydroxyimino)-1-(4-hydroxyphenyl)propan-1-one (1g);** $R_f$ = 0.35 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, MeOD) δ 7.88 (d, $J$ = 8.8 Hz, 2H), 6.80 (d, $J$ = 8.8 Hz, 2H), 2.07 (s, 3H). $^{13}$C NMR (100 MHz, MeOD) δ 192.4, 163.7, 156.8, 134.5, 129.4, 115.8, 10.5. IR (neat) $\nu_{max}$ 3323, 1630, 1577, 1460, 1337, 1162 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_9NO_3$ $[M]^+$ 179.0582, found 178.0588.



To a stirred solution of ketone (492 mg, 3.0 mmol), n-butyl nitrite (0.88 mL, 7.5 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 20 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1h** (481 mg, 83%) as an off-white solid.

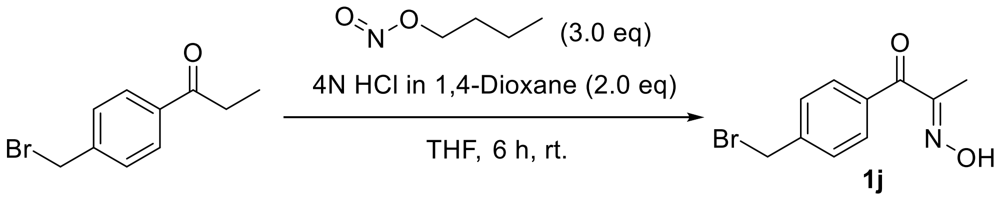
**(E)-2-(hydroxyimino)-1-(4-(hydroxymethyl)phenyl)propan-1-one (1h);** $R_f$= 0.4 (Hex:EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.13 (br s, 1H), 7.84 (d, $J$ = 8.2 Hz, 2H), 7.33 (d, $J$ = 8.2 Hz, 2H), 4.69 (s, 2H), 2.16 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.1, 163.7, 157.1, 132.9, 128.9, 113.6, 55.6, 10.6. IR (neat) $\nu_{max}$ 3441, 3150, 1644, 1606, 1446, 1326 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_{11}NO_3$ $[M]^+$ 193.0739, found 193.0739.



To a stirred solution of ketone (714 mg, 3.0 mmol), n-butyl nitrite (1.05 mL, 9.0 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 8 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 2:1) to afford **1i** (329 mg, 41%) as a white solid.

**(E)-1-(4-benzoylphenyl)-2-(hydroxyimino)propan-1-one (1i);** $R_f$ = 0.45 (Hex:EtOAc = 3:1); $^1$H

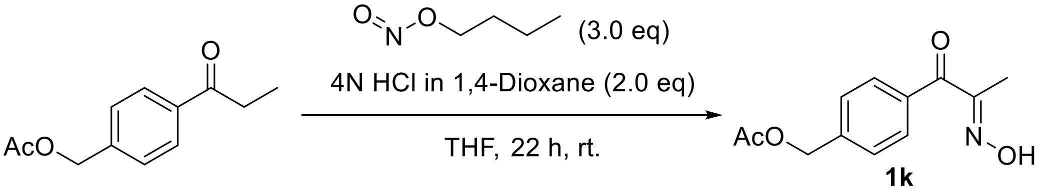
NMR (500 MHz, $CDCl_3$) δ 8.78 (br s, 1H), 7.97-7.94 (m, 2H), 7.83-7.78 (m, 4H), 7.62 (m, 1H), 7.51-7.47 (m, 2H), 2.20 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.6, 191.3, 157.0, 140.6, 139.8, 137.0, 133.1, 130.3, 130.2, 129.6, 128.6, 9.9. IR (neat) $\nu_{max}$ 3319, 1639, 1444, 1400, 1284, 1029 $cm^{-1}$. HRMS[EI+] calcd for $C_{16}H_{13}NO_3$ $[M]^+$ 267.0895, found 267.0893.



**1j**

To a stirred solution of ketone (678 mg, 3.0 mmol), n-butyl nitrite (1.05 mL, 9.0 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 6 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1j** (627 mg, 82%) as a white solid.

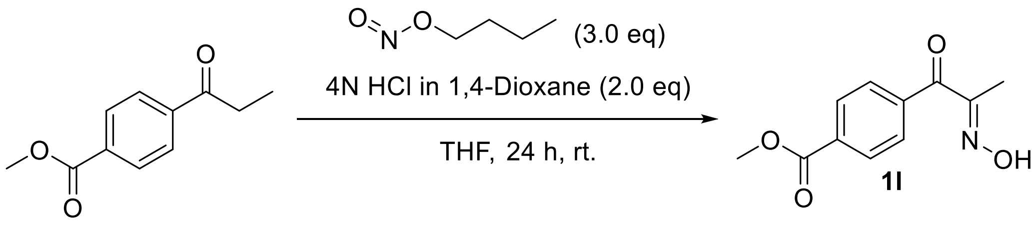
**(E)-1-(4-(bromomethyl)phenyl)-2-(hydroxyimino)propan-1-one (1j);** $R_f$ = 0.6 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.36 (br s, 1H), 7.87 (d, $J$ = 8.3 Hz, 2H), 7.45 (d, $J$ = 8.3 Hz, 2H), 4.50 (s, 2H), 2.17 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.1, 157.1, 142.5, 136.3, 130.9, 128.8, 32.3, 10.2. IR (neat) $\nu_{max}$ 3257, 1668, 1637, 1444, 1315, 1178 $cm^{-1}$. HRMS[EI+] calcd for $C_{10}H_{10}BrNO_2$ $[M]^+$ 254.9895, found 254.9885.



**1k**

To a stirred solution of ketone (618 mg, 3.0 mmol), n-butyl nitrite (1.05 mL, 9.0 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 22 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1k** (480 mg, 68%) as a yellow solid.

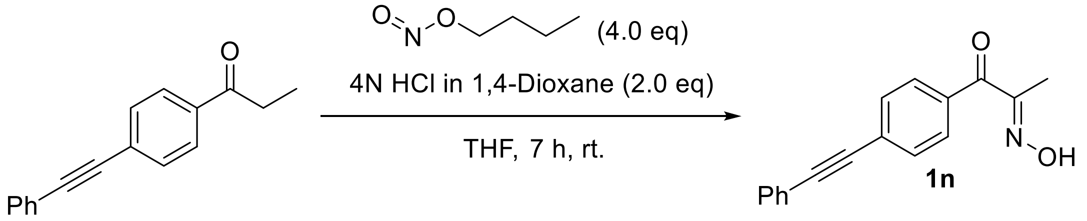
**(E)-4-(2-(hydroxyimino)propanoyl)benzyl acetate (1k);** $R_f$ = 0.4 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.55 (br s, 1H), 7.89 (d, $J$ = 8.3 Hz, 2H), 7.38 (d, $J$ = 8.3 Hz, 2H), 5.14 (s, 2H), 2.17 (s, 3H), 2.12 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.1, 171.7, 157.1, 140.7, 136.3, 130.9, 127.5, 65.7, 21.0, 10.2. IR (neat) $\nu_{max}$ 3368, 1715, 1642, 1606, 1404. 1251 $cm^{-1}$. HRMS[EI+] calcd for $C_{12}H_{13}NO_4$ $[M]^+$ 235.0845, found 235.0856.



**1l**

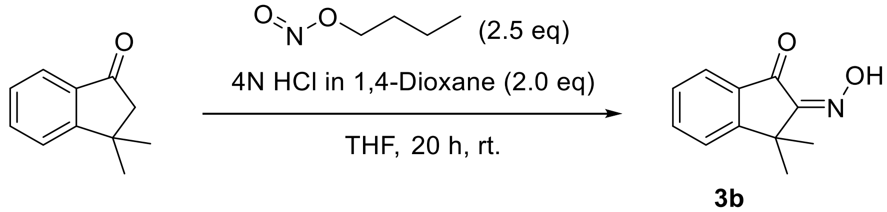
To a stirred solution of ketone (576 mg, 3.0 mmol), n-butyl nitrite (1.05 mL, 9.0 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1l** (464 mg, 70%) as a white solid.

**Methyl (E)-4-(2-(hydroxyimino)propanoyl)benzoate (1l);** $R_f$ = 0.4 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.3, 166.9, 157.2, 140.4, 133.3, 130.3, 129.3, 52.6, 9.9. IR (neat) $\nu_{max}$ 3223, 1728, 1648, 1435, 1275, 1109 cm$^{-1}$. HRMS[EI+] calcd for $C_{11}H_{11}NO_4$ $[M]^+$ 221.0668, found 221.0677.



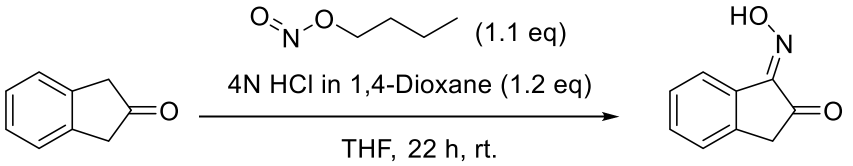
To a stirred solution of ketone (702 mg, 3.0 mmol), n-butyl nitrite (1.4 mL, 12.0 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 7 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **1n** (687 mg, 87%) as a white solid.

**(E)-2-(hydroxyimino)-1-(4-(phenylethynyl)phenyl)propan-1-one (1n);** $R_f$ = 0.35 (Hex:EtOAc = 10:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.56-7.54 (m, 2H), 7.38-7.36 (m, 3H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.8, 157.2, 135.6, 131.9, 131.3, 130.5, 128.9, 128.5, 128.0, 122.8, 92.7, 88.8, 10.2. IR (neat) $\nu_{max}$ 3241, 1653, 1608, 1439, 1314, 1182 cm$^{-1}$. HRMS[EI+] calcd for $C_{17}H_{13}NO_2$ $[M]^+$ 263.0946, found 263.0944.



To a stirred solution of ketone (480 mg, 3.0 mmol), n-butyl nitrite (0.88 mL, 7.5 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.5 mL, 6.0 mmol). After 20 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, filtered through a short pad of silica gel, and concentrated. The crude solid product was recrystallized with ethyl acetate and hexane to afford **3b** (448 mg, 79%) as an off-white solid.

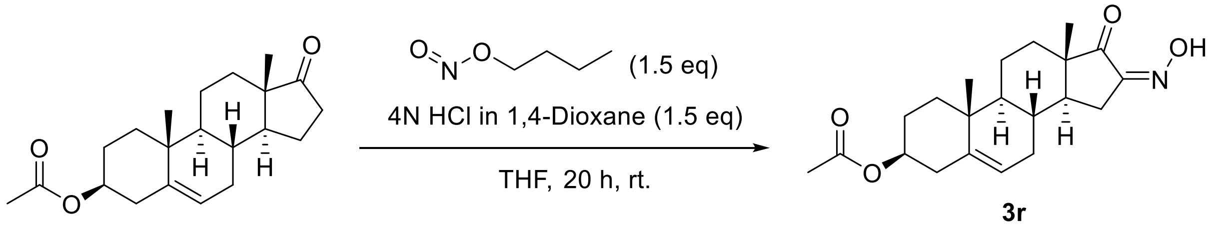
**(Z)-2-(hydroxyimino)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (3b);** $R_f$ = 0.3 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.86 (br s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 1.68 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.4, 159.9, 159.4, 136.6, 135.2, 128.1, 124.2, 123.7, 42.2, 24.8. IR (neat) $\nu_{max}$ 3197, 1715, 1644, 1604, 1457, 1295 cm$^{-1}$. HRMS[EI+] calcd for $C_{11}H_{11}NO_2$ $[M]^+$ 189.0790, found 189.0792.



**3c**

To a stirred solution of ketone (396 mg, 3.0 mmol), n-butyl nitrite (0.38 mL, 3.3 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (0.9 mL, 3.6 mmol). After 22 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 2:1) to afford **3c** (203 mg, 42%) as a brown solid.

**(E)-1-(hydroxyimino)-1,3-dihydro-2H-inden-2-one (3c);** $R_f$ = 0.6 (Hex:EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.6 Hz, 1H), 7.49 (m, 1H), 7.43-7.40 (m, 2H), 3.65 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.0, 150.0, 139.1, 133.0, 132.2, 128.9, 128.1, 125.6, 40.9. IR (neat) $\nu_{max}$ 3075, 1746, 1422, 1324, 1195 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_7NO_2$ [M]$^+$ 161.0477, found 161.0476.

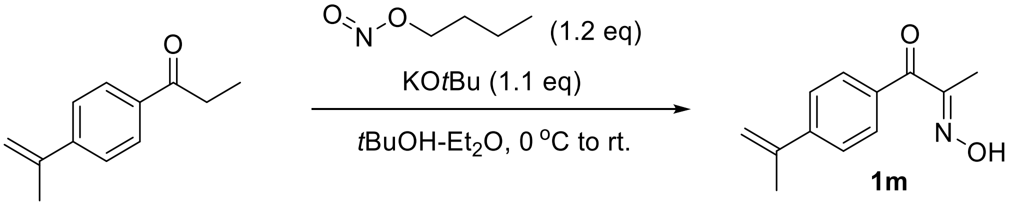


**3r**

To a stirred solution of ketone (991 mg, 3.0 mmol), n-butyl nitrite (0.53 mL, 4.5 mmol) in THF (9.0 mL) was added 4N HCl in 1,4-dioxane (1.13 mL, 4.5 mmol). After 20 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n and extracted with diethy ether (20 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 1:1) to afford **3r** (571 mg, 53%) as an off-white solid.

**(3S,8R,9S,10R,13S,14S,Z)-16-(hydroxyimino)-10,13-di-methyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetrad-ecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (3r);** $R_f$ = 0.3 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (br s, 1H), 5.41 (m, 1H), 4.61 (m, 1H), 2.94 (m, 1H), 2.39-2.28 (m, 2H), 2.91-2.06 (m, 2H), 2.03 (s, 3H), 1.98 (m, 1H), 1.91-1.85 (m, 2H), 1.77 (m, 1H), 1.68-1.55 (m, 2H), 155-1.35 (m, 3H), 1.29-1.05 (m, 3H), 1.05 (s, 3H), 0.97 (s, 3H), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 205.0, 170.8, 156.8, 104.2, 121.6, 73.8, 50.1, 48.8, 46.8, 38.1, 36.95, 36.92, 31.1, 31.0, 30.8, 27.7, 25.6, 21.5, 20.2, 19.5, 14.0. IR (neat) $\nu_{max}$ 3307, 2945, 1740, 1693, 1439, 1267 cm$^{-1}$. HRMS[FAB] calcd for $C_{21}H_{30}NO_4$ [M+H]$^+$ 360.2175, found 360.2179.

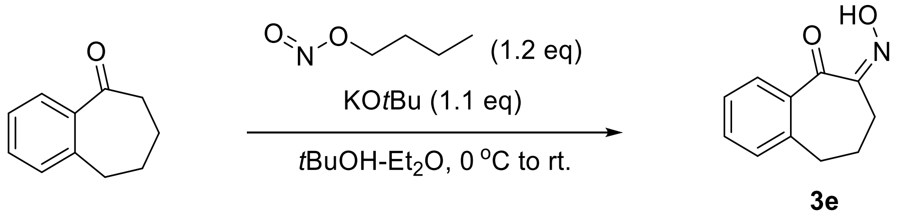
2) Procedure for base-assiated oximation



**1m**

To a stirred solution of ketone (174 mg, 1.0 mmol) and n-butyl nitrite (140 μL, 1.2 mmol) in the mixed solvent of t-BuOH (3.0 mL) and $Et_2O$ (2.0 mL) was added KO$^t$Bu (123 mg, 1.1 mmol) at 0 °C. The resulting slurry was stirred for 4 hours at rt. Then, the mixture was partitioned with water and diethyl ether. The aqueous solution was acidified with 1N HCl (until pH 2-3) and extracted with diethyl ether (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography to afford **1m** (91 mg, 45%) as a white solid.

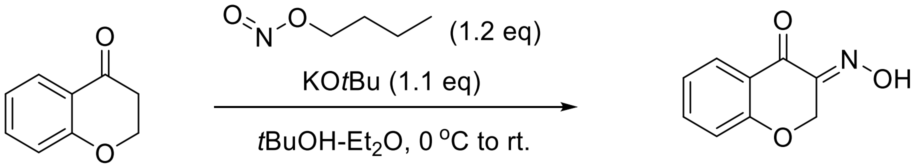
**(E)-2-(hydroxyimino)-1-(4-(prop-1-en-2-yl)phenyl)propan-1-one (1m);** R*f* = 0.3 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (br s, 1H), 7.90-7.86 (m, 2H), 7.53-7.50 (m, 2H), 5.47 (m, 1H), 5.20 (m, 1H), 2.18 (s, 3H), 2.17-2.16 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.2, 157.1, 145.7, 142.5, 135.2, 130.5, 125.3, 114.9, 21.7, 10.3. IR (neat) $\nu_{max}$ 3234, 1659, 1599, 1446, 1309, 1187 cm$^{-1}$. HRMS[EI+] calcd for $C_{12}H_{13}NO_2$ $[M]^+$ 203.0946, found 203.0945.



**3e**

To a stirred solution of ketone (160 mg, 1.0 mmol) and n-butyl nitrite (140 µL, 1.2 mmol) in the mixed solvent of t-BuOH (3.0 mL) and $Et_2O$ (2.0 mL) was added KO$^t$Bu (123 mg, 1.1 mmol) at 0 °C. The resulting slurry was stirred for 4 hours at rt. Then, the mixture was partitioned with water and diethyl ether. The aqueous solution was acidified with 1N HCl (until pH 2-3) and extracted with diethyl ether (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography to afford **3e** (159 mg, 84%) as a white solid.

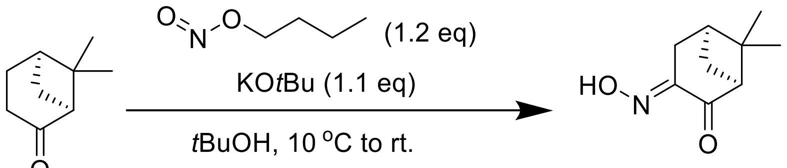
**(Z)-6-(hydroxyimino)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (3e);** R*f* = 0.3 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 9.64 (br s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 2.88 (t, *J* = 6.8 Hz, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.05 (p, *J* = 6.9 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 192.9, 157.2, 140.5, 136.8, 133.7, 129.9, 129.6, 127.3, 32.2, 22.7, 22.4. IR (neat) $\nu_{max}$ 3210, 2935, 1697, 1597, 1455, 1298 cm$^{-1}$ HRMS[EI+] calcd for $C_{11}H_{11}NO_2$ $[M]^+$ 189.0790, found 189.0792.



**3j**

To a stirred solution of ketone (148 mg, 1.0 mmol) and n-butyl nitrite (140 µL, 1.2 mmol) in the mixed solvent of t-BuOH (3.0 mL) and $Et_2O$ (2.0 mL) was added KO$^t$Bu (123 mg, 1.1 mmol) at 0 °C. The resulting slurry was stirred for 4 hours at rt. Then, the mixture was partitioned with water and diethyl ether. The aqueous solution was acidified with 1N HCl (until pH 2-3) and extracted with diethyl ether (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography to afford **3j** (115 mg, 65%) as a light brown solid.

**(Z)-3-(hydroxyimino)chroman-4-one (3j);** R*f* = 0.6 (Hex:EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 10.20 (br s, 1H), 8.01 (dd, *J* = 5.2 and 1.7 Hz, 1H), 7.55 (m, 1H), 7.09 (t, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.04 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 177.2, 161.5, 149.0, 137.2, 127.9, 122.3, 121.5, 118.5, 65.2. IR (neat) $\nu_{max}$ 3195, 1668, 1602, 1462, 1333, 1049 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_7NO_3$ $[M]^+$ 177.0426, found 177.0422.

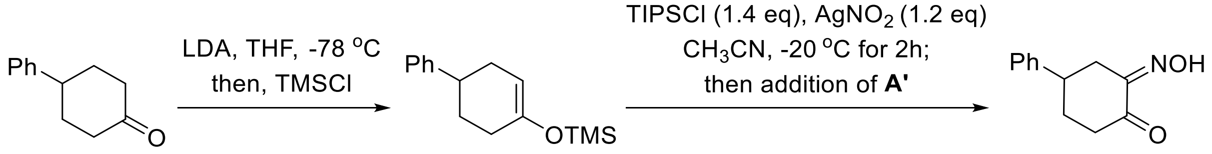


**3o**

To a stirred solution of ketone (138 mg, 1.0 mmol) and n-butyl nitrite (140 µL, 1.2 mmol) in t-BuOH (5.0 mL) was added KO$^t$Bu (123 mg, 1.1 mmol) at 10 °C. The resulting slurry was stirred for 4 hours at rt. Then, the mixture was partitioned with water and diethyl ether. The aqueous solution was acidified with 1N HCl (until pH 2-3) and extracted with diethyl ether (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography to afford the corresponding **3o** (97 mg, 58%) as a white solid.

**(1S,5S,Z)-3-(hydroxyimino)-6,6-dimethylbicyclo[3.1.1]heptan-2-one (3o);** R$_f$ = 0.55 (Hex:EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 10.29 (br s, 1H), 2.89-2.80 (m, 2H), 2.76 (m, 1H), 2.71 (m, 1H), 2.33 (m, 1H), 1.53 (d, *J* = 8.7 Hz, 1H), 1.38 (s, 3H), 0.90 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 198.6, 152.8, 56.5, 41.8, 37.7, 31.1, 28.2, 27.9, 26.4. IR (neat) $\nu_{max}$ 3290, 2935, 1424, 1213, 1031 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_{13}NO_2$ $[M]^+$ 167.0946, found 167.0934.

3) Procedure using Yamamoto's method[11]



**A** **A'** **3k**

Step 1: To a stirred solution of **A** (174 mg, 1.0 mmol) in THF (3.0 mL) was added a solution of LDA (1.0 M in THF, 1.1 mL, 1.1 mmol) at -78 °C. The reaction mixture was additionally stirred for 0.5 h and TMSCl (0.15 mL, 1.2 mmol) was added to the solution of lithium enolate at the same temperature. Then, the reaction mixture was slowly warmed to 0 °C and quenched with sat. $NaHCO_3$ sol'n and extracted with hexane (10 X 3 mL). The organic solution was dried over $MgSO_4$, concentrated, and directly used for the next reaction without further purification.

Step 2: To a stirred solution of silver nitrite (185 mg, 1.2 mmol) in dry $CH_3CN$ (5 mL) was added dropwise TIPSCl (270 mg, 1.4 mmol) in $CH_3CN$ (1.0 mL) at -20 °C. The resulting slurry was stirred additionally for 2 h under darkness and treated with the silylenol ether **A'** freshly prepared in step 1 in $CH_3CN$ (0.5 mL) at -20 °C. After 2 h, the reaction mixture was quenched with 1:1 mixture of brine and sat. $NaHCO_3$ sol'n and extracted with EtOAc (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **3k** (132 mg, 65% for 2 steps) as a white solid.

**2-(hydroxyimino)-4-phenylcyclohexan-1-one (3k);** R$_f$ = 0.45 (Hex:EtOAc = 1:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 9.96 (br s, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29-7.26 (m, 3H), 3.40 (m, 1H), 3.12 (m, 1H), 2.80 (m, 1H), 2.72-2.61 (m, 2H), 2.22 (m, 1H), 2.15 (m, 1H), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.8, 153.2,

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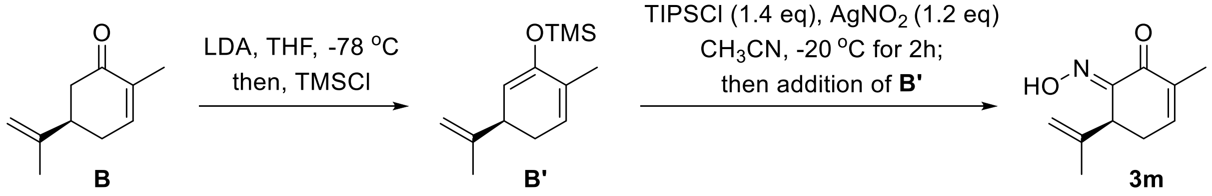
[11] Baidya, M.; Yamamoto, H. *J. Am. Chem. Soc.* **2011**, *133*, 13880.

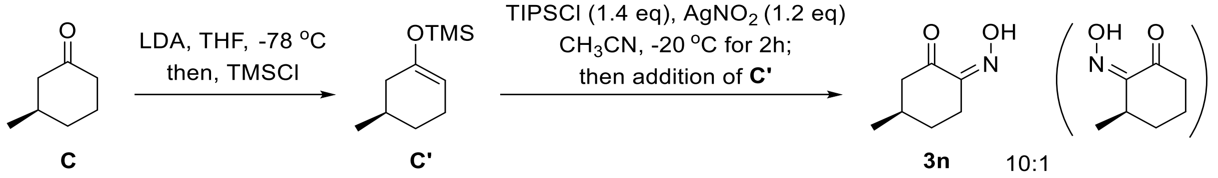
143.8, 128.9, 127.1, 126.7, 39.9, 39.3, 32.7, 29.6. IR (neat) $\nu_{max}$ 3279, 1690, 1568, 1393, 1016 cm$^{-1}$. HRMS[EI+] calcd for $C_{12}H_{13}NO_2$ [M]$^+$ 203.0946, found 203.0946.



Step 1: To a stirred solution of **B** (150 mg, 1.0 mmol) in THF (3.0 mL) was added a solution of LDA (1.0 M in THF, 1.1 mL, 1.1 mmol) at -78 °C. The reaction mixture was additionally stirred for 0.5 h and TMSCl (0.15 mL, 1.2 mmol) was added to the solution of lithium enolate at the same temperature. Then, the reaction mixture was slowly warmed to 0 °C and quenched with sat. $NaHCO_3$ sol'n and extracted with hexane (10 X 3 mL). The organic solution was dried over $MgSO_4$, concentrated, and directly used for the next reaction without further purification.

Step 2: To a stirred solution of silver nitrite (185 mg, 1.2 mmol) in dry $CH_3CN$ (5 mL) was added dropwise TIPSCl (270 mg, 1.4 mmol) in $CH_3CN$ (1.0 mL) at -20 °C. The resulting slurry was stirred additionally for 2h under darkness and treated with the silylenol ether **B'** freshly prepared in step 1 in $CH_3CN$ (0.5 mL) at -20 °C. After 2h, the reaction mixture was quenched with 1:1 mixture of brine and sat. $NaHCO_3$ sol'n and extracted with EtOAc (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **3m** (75 mg, 42% for 2 steps) as a light brown solid.

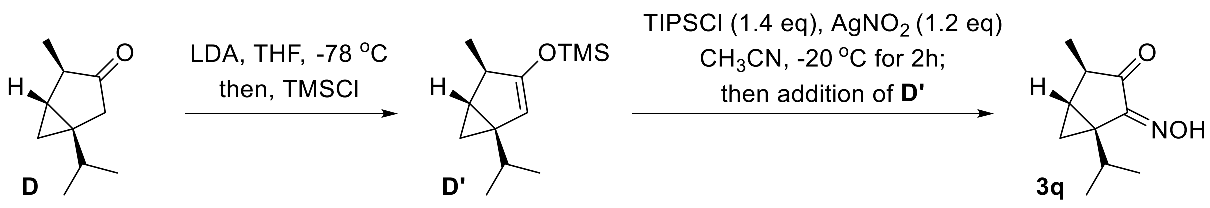
**6-(hydroxyimino)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one (3m);** $R_f$ = 0.5 (Hex:EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 10.51 (br s, 1H), 6.80 (m, 1H), 4.83 (s, 1H), 4.67 (s, 1H), 4.40 (d, $J$ = 6.5 Hz, 1H), 2.70 (m, 1H), 2.59 (m, 1H), 1.87-1.86 (m, 3H), 1.75 (s, 3H), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 184.3, 154.0, 144.7, 142.5, 137.1, 112.9, 40.1, 28.5, 21.9, 16.0. IR (neat) $\nu_{max}$ 3250, 2918, 1648, 1576, 1406, 1366 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_{13}NO_2$ [M]$^+$ 179.0946, found 179.0940.



Step 1: To a stirred solution of **C** (112 mg, 1.0 mmol) in THF (3.0 mL) was added a solution of LDA (1.0 M in THF, 1.1 mL, 1.1 mmol) at -78 °C. The reaction mixture was additionally stirred for 0.5 h and TMSCl (0.15 mL, 1.2 mmol) was added to the solution of lithium enolate at the same temperature. Then, the reaction mixture was slowly warmed to 0 °C and quenched with sat. $NaHCO_3$ sol'n and extracted with hexane (10 X 3 mL). The organic solution was dried over $MgSO_4$, concentrated, and directly used for the next reaction without further purification.

Step 2: To a stirred solution of silver nitrite (185 mg, 1.2 mmol) in dry $CH_3CN$ (5 mL) was added dropwise TIPSCl (270 mg, 1.4 mmol) in $CH_3CN$ (1.0 mL) at -20 °C. The resulting slurry was stirred additionally for 2h under darkness and treated with the silylenol ether **C'** freshly prepared in step 1 in $CH_3CN$ (0.5 mL) at -20 °C. After 2h, the reaction mixture was quenched with 1:1 mixture of brine and sat. $NaHCO_3$ sol'n and extracted with EtOAc (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **3n** (106 mg, 75% for 2 steps, regioisomeric ratio = 10:1) as a white solid.

**2-(hydroxyimino)-5-methylcyclohexan-1-one (3n);** $R_f$ = 0.45 (Hex:EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 10.30 (br s, 1H), 3.10 (m, 1H), 2.68 (m, 1H), 2.47 (m, 1H), 2.15 (m, 1H), 2.04 (m, 1H), 1.95 (m, 1H), 1.43 (m, 1H), 1.05 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 196.5, 153.6, 49.0, 29.6, 29.5, 23.8, 21.4. IR (neat) $\nu_{max}$ 3183, 1701, 1600, 1418, 1278 cm$^{-1}$. HRMS[EI+] calcd for $C_7H_{11}NO_2$ $[M]^+$ 141.0790, found 141.0791.

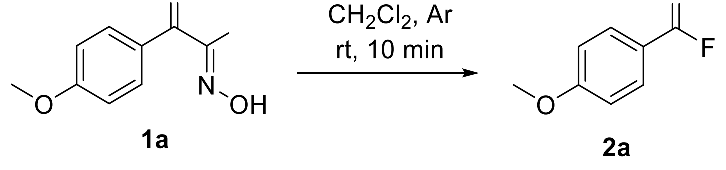


Step 1: To a stirred solution of **D** (152 mg, 1.0 mmol) in THF (3.0 mL) was added a solution of LDA (1.0 M in THF, 1.1 mL, 1.1 mmol) at -78 °C. The reaction mixture was additionally stirred for 0.5 h and TMSCl (0.15 mL, 1.2 mmol) was added to the solution of lithium enolate at the same temperature. Then, the reaction mixture was slowly warmed to 0 °C and quenched with sat. $NaHCO_3$ sol'n and extracted with hexane (10 X 3 mL). The organic solution was dried over $MgSO_4$, concentrated, and directly used for the next reaction without further purification.

Step 2: To a stirred solution of silver nitrite (185 mg, 1.2 mmol) in dry $CH_3CN$ (5 mL) was added dropwise TIPSCl (270 mg, 1.4 mmol) in $CH_3CN$ (1.0 mL) at -20 °C. The resulting slurry was stirred additionally for 2h under darkness and treated with the silylenol ether **D'** freshly prepared in step 1 in $CH_3CN$ (0.5 mL) at -20 °C. After 2h, the reaction mixture was quenched with 1:1 mixture of brine and sat. $NaHCO_3$ sol'n and extracted with EtOAc (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **3q** (109 mg, 60% for 2 steps) as a light yellow solid.

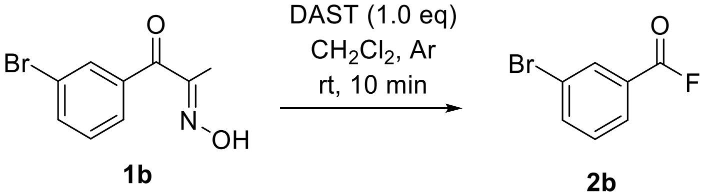
**(1S,4R,5R)-2-(hydroxyimino)-1-isopropyl-4,5-dimethylbicyclo[3.1.0]hexan-3-one (3q);** $R_f$ = 0.4 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 9.78 (br s, 1H), 2.87 (m, 1H), 2.46-2.41 (q, $J$ = 7.5 Hz, 1H), 1.44 (m, 1H), 1.37 (m, 1H), 1.23 (d, $J$ = 7.5 Hz, 3H), 1.03 (d, $J$ = 6.6 Hz, 3H), 0.75 (d, $J$ = 6.9 Hz, 3H), 0.59 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.9, 156.2, 44.5, 35.6, 26.1, 22.4, 21.7, 19.3, 17.6, 17.5. IR (neat) $\nu_{max}$ 3239, 2964, 1740, 1636, 1449, 1296 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_{15}NO_2$ $[M]^+$ 181.1103, found 181.1102.

## Procedure for DAST-mediated fluorinative C-C bond cleavage



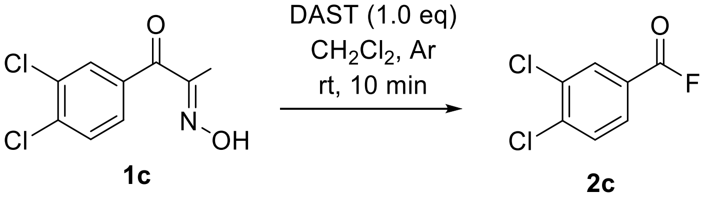
A 10 mL round bottom flask was charged with **1a** (58 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane) to afford **2a** (40 mg, 87%) as a pale yellow oil.

**4-methoxybenzoyl fluoride** (**2a**); $R_f$ = 0.5 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.3 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 15.99 (s, 1F), This spectral data is in agreement with the reported.[12]



A 10 mL round bottom flask was charged with **1b** (72 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane) to afford **2b** (49 mg, 81%) as a colorless oil.

**3-bromobenzoyl fluoride** (**2b**); $R_f$ = 0.65 (Hex:EtOAc = 20:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 19.08 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.2 (d, $J_{C,F}$ = 343 Hz), 138.5, 134.4 (d, $J_{C,F}$ = 4 Hz), 130.7 (d, $J_{C,F}$ = 1 Hz), 130.0 (d, $J_{C,F}$ = 4 Hz), 127.0 (d, $J_{C,F}$ = 62 Hz), 123.2 (d, $J_{C,F}$ = 1 Hz). IR (neat) $\nu_{max}$ 2957, 2857, 1815, 1238, 1029, 734 cm$^{-1}$. HRMS[EI+] calcd for $C_7H_4BrFO$ $[M]^+$ 201.9430, found 201.9425.



A 10 mL round bottom flask was charged with **1c** (70 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane) to afford **2c** (42 mg, 73%) as a colorless oil.

**3,4-dichlorobenzoyl fluoride (2c)**; $R_f$ = 0.65 (Hex:EtOAc = 50:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 8.2 and 2.1 Hz, 1H), 7.63 (dd, *J* = 8.3 and 3.4 Hz, 1H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 19.16 (s, 1F), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.7 (d, $J_{C,F}$ = 342 Hz), 140.7, 134.1,

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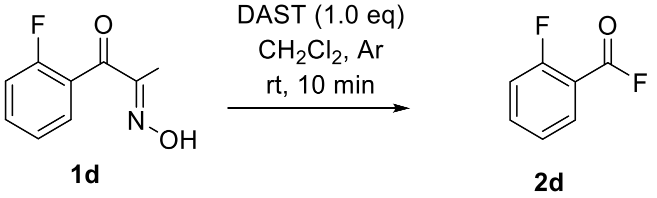
[12] Arisawa, M.; Igarashi, Y.; Kobayashi, H.; Yamada, T.; Bando, K.; Ichikawa, T.; Yamaguchi, M. *Tetrahedron* **2011**, *67*, 7846.

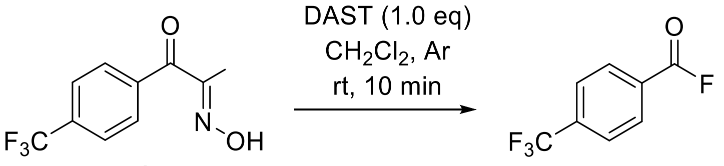
133.2 (d, $J_{C,F}$ = 3 Hz), 131.5 (d, $J_{C,F}$ = 1 Hz), 130.3 (d, $J_{C,F}$ = 3 Hz), 124.8 (d, $J_{C,F}$ = 63 Hz), IR (neat) $\nu_{max}$ 3039, 1817, 1611, 1467, 1270, 1054 cm$^{-1}$. HRMS[EI+] calcd for $C_7H_3Cl_2FO$ [M]$^+$ 191.9545, found 191.9546.



**1d** **2d**

A 10 mL round bottom flask was charged with **1d** (54 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane) to afford **2d** (34 mg, 80%) as a colorless oil.

**2-fluorobenzoyl fluoride (2d)**; $R_f$ = 0.5 (Hex:EtOAc = 20:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (t, $J$ = 6.7 Hz, 1H), 7.72 (m, 1H), 7.32 (t, $J$ = 7.7 Hz, 1H), 7.26 (t, $J$ = 9.3 Hz, 1H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 31.56 (s, 1F), 106.2 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.3 (dd, $J_{C,F}$ = 264 and 2 Hz), 154.1 (dd, $J_{C,F}$ = 342 and 4 Hz), 137.5 (d, $J_{C,F}$ = 9 Hz), 133.5 (d, $J_{C,F}$ = 3 Hz), 124.8 (d, $J_{C,F}$ = 4 Hz), 117.7 (dd, $J_{C,F}$ = 19 and 2 Hz), 113.5 (dd, $J_{C,F}$ = 113 and 53 Hz). IR (neat) $\nu_{max}$ 3089, 1819, 1613, 1585, 1490, 1289 cm$^{-1}$. HRMS[EI+] calcd for $C_7H_4F_2O$ [M]$^+$ 142.0230, found 142.0222.



**1e** **2e**

A 10 mL round bottom flask was charged with **1e** (69 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane) to afford **2e** (42 mg, 73%) as a colorless oil.

**4-(trifluoromethyl) benzoyl fluoride (2e)**; $R_f$ = 0.6 (Hex:EtOAc = 50:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, $J$ = 8.5 Hz, 2H), 7.81 (d, $J$ = 8.5 Hz, 2H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 19.9 (s, 1F), −63.5 (s, 3F), This spectral data is in agreement with the reported.[13]

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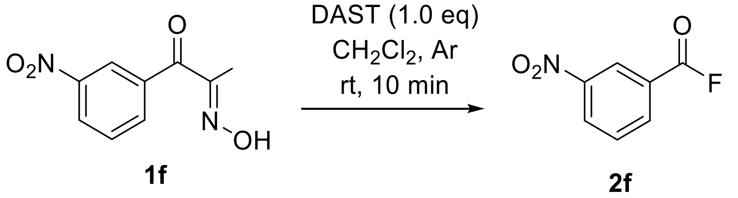
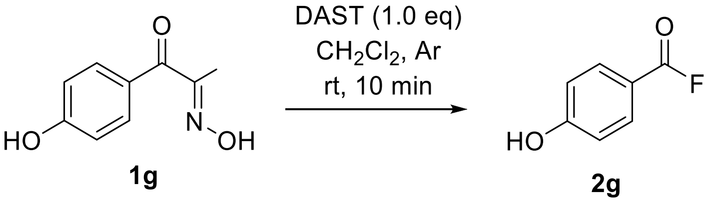
[13] Stavber, S.; Planinšek, Z.; Zupan, M. *J. Org. Chem.* **1992**, *57*, 5334.



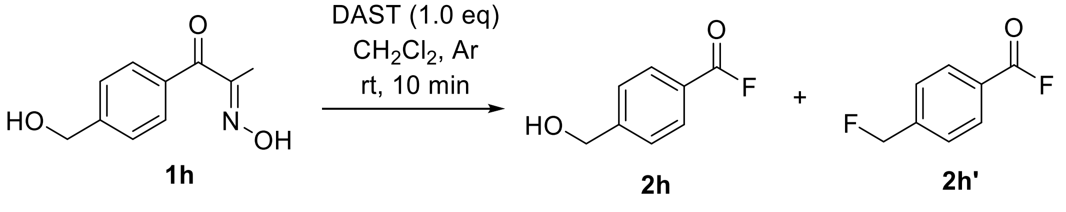
A 10 mL round bottom flask was charged with **1f** (62 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 50:1) to afford **2f** (42 mg, 83%) as a white solid.

**3-nitrobenzoyl fluoride (2f)**; $R_f$ = 0.4 (Hex:EtOAc = 10:1); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.89 (t, $J$ = 2.0 Hz, 1H), 8.57 (m, 1H), 8.39 (d, $J$ = 7.8 Hz, 1H), 7.79 (td, $J$ = 7.9 and 1.3 Hz, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ 20.19 (s, 1F). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 155.3 (d, $J_{C,F}$ = 343 Hz), 148.5, 136.7 (d, $J_{C,F}$ = 4 Hz), 130.5, 129.7, 126.8 (d, $J_{C,F}$ = 65 Hz), 126.3 (d, $J_{C,F}$ = 4 Hz). IR (neat) $\nu_{max}$ 3094, 1813, 1584, 1535, 1350, 1247cm$^{-1}$. HRMS[EI+] calcd for $C_7H_4FNO_3$ $[M]^+$ 169.0175, found 169.0165.



A 10 mL round bottom flask was charged with **1g** (54 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **2g** (31 mg, 74%) as a white solid.

**4-hydroxybenzoyl fluoride (2g)**; $R_f$ = 0.25 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.97 (d, $J$ = 8.8 Hz, 2H), 6.94 (d, $J$ = 7.2 Hz, 2H), 5.80 (s, 1H), $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ 18.2 (s, 1F). This spectral data is in agreement with the reported.[14]



A 10 mL round bottom flask was charged with **1h** (58 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under

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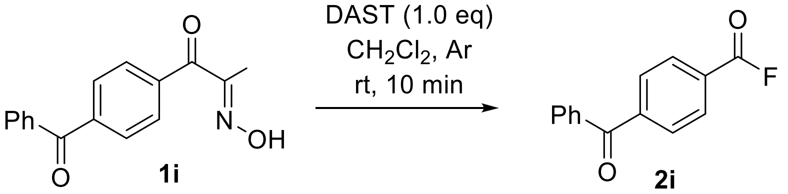
[14] Munoz, S. B.; Dang, H.; Ispizua-Rodriguez, X.; Mathew, T.; Prakash, G. K. S. *Org. Lett.* **2019**, *21*, 1659.

Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 1:1) to afford **2h** (19 mg, 41%) and **2h'** (14 mg, 30%).

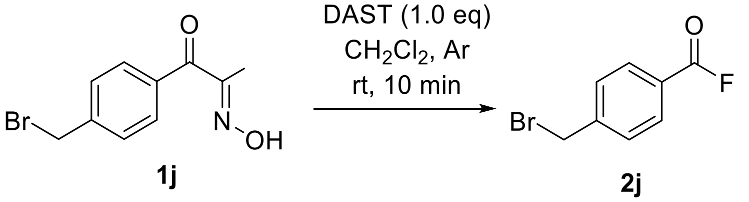
**4-(hydroxymethyl) benzoyl fluoride (2h)**; white solid; $R_f$ = 0.25 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, $J$ = 8.3 Hz , 2H), 7.53 (d, $J$ = 7.5 Hz , 2H), 4.83 (s, 2H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 18.18 (s, 1F), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4 (d, $J_{C,F}$ = 341 Hz), 148.9, 131.8 (d, $J_{C,F}$ = 4 Hz), 126.9 (d, $J_{C,F}$ = 1 Hz), 124.0 (d, $J_{C,F}$ = 60 Hz), 64.5. IR (neat) $\nu_{max}$ 3414, 2960, 1808, 1714, 1612, 1419, 1273 cm$^{-1}$. HRMS[EI+] calcd for $C_8H_7FO_2$ $[M]^+$ 154.0430, found 154.0425.

**4-(fluoromethyl) benzoyl fluoride (2h')**; colorless oil; $R_f$ = 0.55 (Hex:EtOAc = 10:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, $J$ = 7.5 Hz , 2H), 7.51 (d, $J$ = 7.5 Hz , 2H), 5.49 (d, $J$ = 46.8 Hz, 2H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 18.52 (s, 1F), - 216.09 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.1 (d, $J_{C,F}$ = 342 Hz), 144.1 (d, $J_{C,F}$ = 17 Hz), 131.8 (d, $J_{C,F}$ = 4 Hz), 126.8 (dd, $J_{C,F}$ = 5 and 1 Hz), 125.0 (dd, $J_{C,F}$ = 59 and 2 Hz), 83.3 (d, $J_{C,F}$ = 169 Hz). IR (neat) $\nu_{max}$ 2955, 1811, 1615, 1257, 1038, 1010 cm$^{-1}$. HRMS[EI+] calcd for $C_8H_6F_2O$ $[M]^+$ 156.0387, found 156.0383.



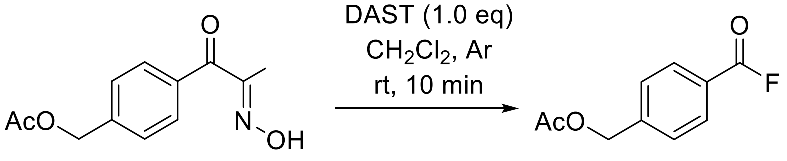
A 10 mL round bottom flask was charged with **1i** (80 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1) to afford **2i** (65 mg, 95%) as a white solid.

**4-benzoylbenzoyl fluoride (2i);** $R_f$ = 0.5 (Hex:EtOAc = 10:1); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, $J$ = 8.4 Hz , 2H), 7.92-7.89 (m, 2H), 7.82-7.79 (m , 2H), 7.65 (m, 1H), 7.55-7.49 (m, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 19.97 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.5, 156.7 (d, $J_{C,F}$ = 343 Hz), 143.6, 136.5, 133.5, 131.5 (d, $J_{C,F}$ = 3 Hz), 130.26, 130.27, 128.7, 127.9 (d, $J_{C,F}$ = 62 Hz). IR (neat) $\nu_{max}$ 1819, 1805, 1745, 1317, 1026 cm$^{-1}$. HRMS[EI+] calcd for $C_{14}H_9FO_2$ $[M]^+$ 228.0587, found 228.0592.



A 10 mL round bottom flask was charged with **1j** (77 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 50:1) to afford **2j** (57 mg, 87%) as a white solid.

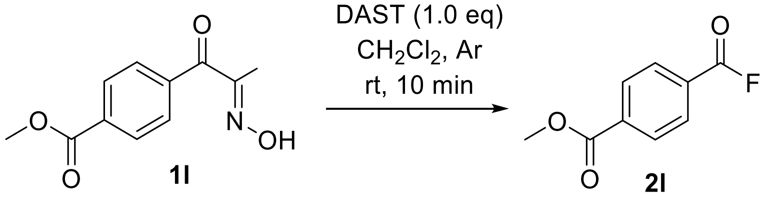
**4-(bromomethyl) benzoyl fluoride (2j)**; $R_f$ = 0.4 (Hex:EtOAc = 50:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, $J$ = 8.5 Hz , 2H), 7.55 (d, $J$ = 8.5 Hz , 2H), 4.50 (s, 2H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 18.63 (s, 1F), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, $J_{C,F}$ = 342 Hz), 145.4, 132.0 (d, $J_{C,F}$ = 4 Hz), 129.8 (d, $J_{C,F}$ = 1 Hz), 124.9 (d, $J_{C,F}$ = 61 Hz), 31.5. IR (neat) $\nu_{max}$ 3060, 1808, 1636, 1578, 1259, 1012 cm$^{-1}$. HRMS[EI+] calcd for $C_8H_6BrFO$ [M]$^+$ 215.9586, found 215.9589.



**1k** **2k**

A 10 mL round bottom flask was charged with **1k** (71 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1) to afford **2k** (51 mg, 86%) as a white solid.

**4-(fluorocarbonyl) benzyl acetate (2k)**; $R_f$ = 0.4 (Hex:EtOAc = 10:1); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, $J$ = 8.3 Hz , 2H), 7.27 (d, $J$ = 8.3 Hz , 2H), 5.19 (s, 2H), 2.14 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 18.4. (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.7, 157.2 (d, $J_{C,F}$ = 342 Hz), 143.9, 131.8 (d, $J_{C,F}$ = 4 Hz), 128.2 (d, $J_{C,F}$ = 1 Hz), 124.7(d, $J_{C,F}$ = 61 Hz), 65.2, 20.9. IR (neat) $\nu_{max}$ 1804, 1745, 1511, 1419, 1122, 1029 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_9FO_3$ [M]$^+$ 196.0536, found 196.0533.

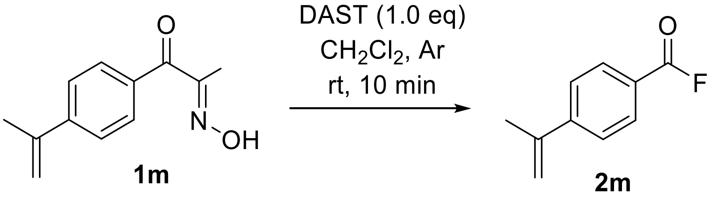


**1l** **2l**

A 10 mL round bottom flask was charged with **1l** (66 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 3:1) to afford **2l** (41 mg, 74%) as a white solid.

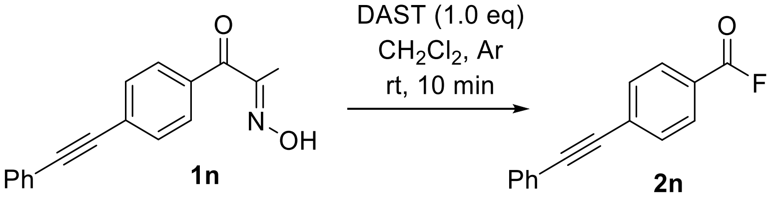
**methyl 4-(fluorocarbonyl) benzoate (2l);** $R_f$ = 0.5 (Hex:EtOAc = 1:3); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, $J$ = 8.0 Hz , 2H), 8.12 (d, $J$ = 8.5 Hz , 2H), 3.97 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 20.07

(s, 1F). This spectral data is in agreement with the reported.[15]



A 10 mL round bottom flask was charged with **1m** (61 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 50:1) to afford **2m** (40 mg, 82%) as a white solid.

**4-(prop-1-en-2-yl) benzoyl fluoride (2m)**; $R_f$ = 0.5 (Hex:EtOAc = 50:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, $J$ = 6.6 Hz , 2H), 7.59 (d, $J$ = 7.2 Hz , 2H), 5.52 (m, 1H), 5.27 (m, 1H), 2.18 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 17.89 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4 (d, $J_{C,F}$ = 341 Hz), 148.2, 142.1, 131.6 (d, $J_{C,F}$ = 4 Hz), 126.2, 123.6 (d, $J_{C,F}$ = 61 Hz), 116.1, 21.6. IR (neat) $\nu_{max}$ 2978, 1807, 1462, 1159, 1038 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_9FO$ $[M]^+$ 164.0637, found 164.0652.



A 10 mL round bottom flask was charged with **1n** (79 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 50:1) to afford **2n** (61 mg, 91%) as a white solid.

**4-(phenylethynyl) benzoyl fluoride (2n);** $R_f$ = 0.5 (Hex:EtOAc = 50:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, $J$ = 6.6 Hz , 2H), 7.66 (d, $J$ = 7.5 Hz , 2H), 7.57-7.55 (m, 2H), 7.40-7.38 (m, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 18.29 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.0 (d, $J_{C,F}$ = 341 Hz), 132.2, 132.0, 131.5 (d, $J_{C,F}$ = 3 Hz), 130.8, 129.3, 128.6, 124.1 (d, $J_{C,F}$ = 61 Hz), 122.4, 94.4, 88.1. IR (neat) $\nu_{max}$ 2216, 1812, 1601, 1255, 1247 cm$^{-1}$. HRMS[EI+] calcd for $C_{15}H_9FO$ $[M]^+$ 224.0637, found.224.0645.

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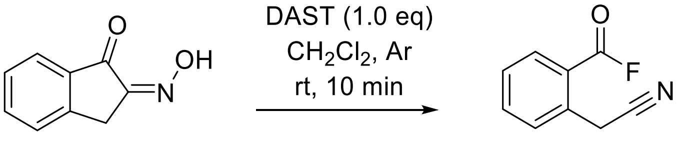
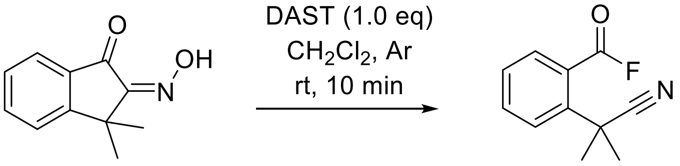
[15] Boreux, A.; Indukuri, K.; Gagosz, F.; Riant, O. *ACS Catal.* **2017**, *7*, 8200.



**3a** **4a**

A 10 mL round bottom flask was charged with **3a** (48 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4a** (41 mg, 83%) as a white solid.

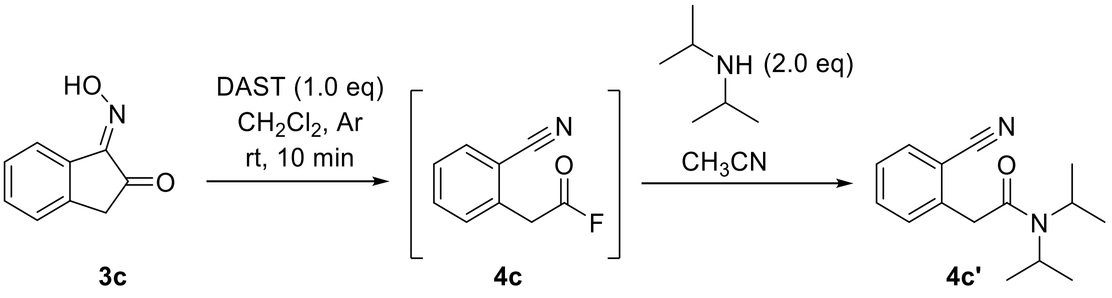
**2-(cyanomethyl) benzoyl fluoride (4a)**; $R_f$ = 0.25 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J$ = 8.1 Hz , 1H), 7.75 (m, 2H), 7.54 (m, 1H), 4.23 (s, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 27.81 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.1 (d, $J_{C,F}$ = 343 Hz), 135.9, 134.8 (d, $J_{C,F}$ = 8 Hz), 133.3 (d, $J_{C,F}$ = 1 Hz), 130.6 (d, $J_{C,F}$ = 4 Hz), 129.1, 122.8 (d, $J_{C,F}$ = 57 Hz), 116.9, 23.2. IR (neat) $\nu_{max}$ 2922, 2252, 1795, 1577, 1411, 1236 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_6FNO$ $[M]^+$ 163.0433, found 163.0453.



**3b** **4b**

A 10 mL round bottom flask was charged with **3b** (57 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4b** (42 mg, 73%) as a white solid.

**2-(2-cyanopropan-2-yl) benzoyl fluoride (4b);** $R_f$ = 0.25 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J$ = 7.9 Hz , 1H), 7.68-7.66 (m , 2H), 7.49 (t, $J$ = 7.4 Hz, 1H), 1.91 (s, 6H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 39.70 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, $J_{C,F}$ = 347 Hz), 143.0 (d, $J_{C,F}$ = 6 Hz), 134.6, 133.1 (d, $J_{C,F}$ = 1 Hz), 128.5, 127.1 (d, $J_{C,F}$ = 3 Hz), 124.7 (d, $J_{C,F}$ = 59 Hz), 123.7, 36.7, 28.74, 28.72. IR (neat) $\nu_{max}$ 2984, 2227, 2161, 1808, 1573, 1220 cm$^{-1}$. HRMS[EI+] calcd for $C_{11}H_{10}FNO$ $[M]^+$ 191.0746, found 191.0761.

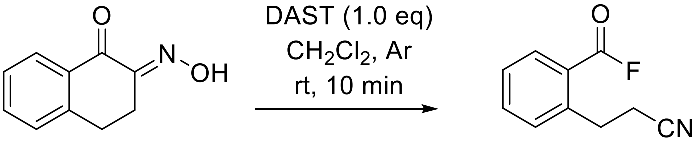


**3c** **4c** **4c'**

A 10 mL round bottom flask was charged with **3c** (48 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under

Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$ and concentrated. The crude product was dissolved in $CH_3CN$ (3.0 mL) and treated with diisopropylamine (84 μL, 0.6 mmol). After 5 min, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with $H_2O$ (10 mL). The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1) to afford **4c'** (50 mg, 68%) as a light brown solid.

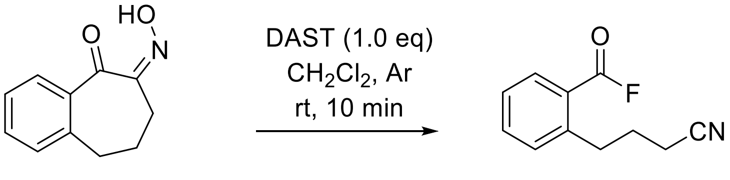
**2-(2-cyanophenyl)-N,N-diisopropylacetamide (4c');** $R_f$ = 0.3 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.7 and 1.4 Hz, 1H), 7.55 (td, *J* = 7.7 and 1.4 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.34 (td, *J* = 7.7 and 1.4 Hz, 1H), 4.02 (p, *J* = 6.7 Hz, 1H), 3.88 (s, 2H), 3.47 (s , 1H), 1.41 (d, *J* = 6.7 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.8, 140.1, 132.8, 132.7, 130.5, 127.3, 117.9, 113.2, 49.3, 46.3, 40.8, 20.9, 20.6. IR (neat) $\nu_{max}$ 2962, 2214, 1644, 1448, 1342, 1280 $cm^{-1}$. HRMS[EI+] calcd for $C_{15}H_{20}N_2O$ $[M]^+$ 244.1576, found 244.1582.



**3d** **4d**

A 10 mL round bottom flask was charged with **3d** (53 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 7:1 to 5:1) to afford **4d** (42 mg, 79%) as a light orange solid.

**2-(2-cyanoethyl)benzoyl fluoride (4d);** $R_f$ = 0.3 (Hex:EtOAc = 7:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz , 1H), 7.68 (t, *J* = 7.5 Hz , 1H), 7.47 (t, *J* = 7.0 Hz , 2H), 3.34 (t, *J* = 7.0 Hz , 2H), 2.73 (t, *J* = 7.0 Hz , 2H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 28.68 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.4 (d, $J_{C,F}$ = 344 Hz), 143.0 (d, $J_{C,F}$ = 9 Hz), 135.6, 133.2 (d, $J_{C,F}$ = 2 Hz), 132.4 (d, $J_{C,F}$ = 4 Hz), 128.3, 123.2 (d, $J_{C,F}$ = 56 Hz), 118.9, 30.5, 18.5. IR (neat) $\nu_{max}$ 2247, 1795, 1597, 1453, 1231 $cm^{-1}$. HRMS[EI+] calcd for $C_{10}H_8FNO$ $[M]^+$ 177.0590, found 177.0580.

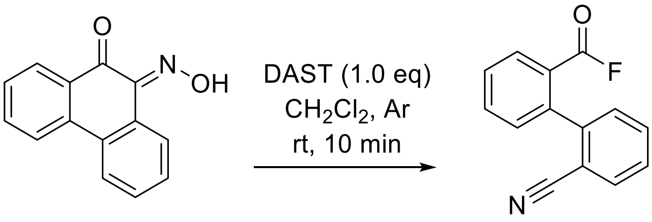


**3e** **4e**

A 10 mL round bottom flask was charged with **3e** (57 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4e** (57 mg, 99%) as a colorless oil.

**2-(3-cyanopropyl)benzoyl fluoride (4e);** $R_f$ = 0.3 (Hex:EtOAc = 10:1); $^1$H NMR (500 MHz, $CDCl_3$)

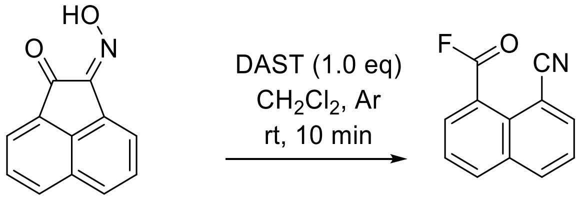
δ 8.03 (d, *J* = 7.9 Hz , 1H), 7.62 (t, *J* = 7.6 Hz , 1H), 7.42-7.37 (m, 2H), 3.15 (t, *J* = 7.8 Hz , 2H), 2.41 (t, *J* = 7.1 Hz , 2H), 1.98 (p, *J* = 7.6 Hz , 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 29.39 (s, 1F), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.3 (d, $J_{C,F}$ = 344 Hz), 145.4 (d, $J_{C,F}$ = 8 Hz), 135.2, 133.1 (d, $J_{C,F}$ = 2 Hz), 131.9 (d, $J_{C,F}$ = 5 Hz), 127.4, 123.2 (d, $J_{C,F}$ = 56 Hz), 119.4, 33.5, 26.6, 17.0. IR (neat) $\nu_{max}$ 2946, 2229, 1803, 1599, 1231 cm$^{-1}$. HRMS[EI+] calcd for $C_{11}H_{10}FNO$ $[M]^+$ 191.0746, found 191.0761.



**3f** **4f**

A 10 mL round bottom flask was charged with **3f** (67 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4f** (52 mg, 77%) as a colorless oil.

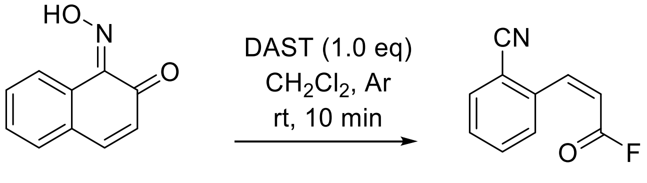
**2'-cyano-[1,1'-biphenyl]-2-carbonyl fluoride (4f);** $R_f$ = 0.35 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.0 and 1.4 Hz , 1H), 7.79-7.75 (m, 2H), 7.68-7.60 (m, 2H), 7.51 (td, *J* = 7.8 and 1.2 Hz, 1H), 7.42 (m, 1H), 7.37 (m, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 29.28 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.2 (d, $J_{C,F}$ = 344 Hz), 144.1, 142.0 (d, $J_{C,F}$ = 4 Hz), 134.8, 132.8, 132.8, 132.6, 131.9 (d, $J_{C,F}$ = 3 Hz), 129.6, 129.4, 128.4, 124.1 (d, $J_{C,F}$ = 58 Hz), 117.8, 112.4. IR (neat) $\nu_{max}$ 2181, 1799, 1439, 1227, 1007 cm$^{-1}$. HRMS[EI+] calcd for $C_{14}H_8FNO$ $[M]^+$ 225.0590, found 225.0577.



**3g** **4g**

A 10 mL round bottom flask was charged with **3g** (59 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 3:1) to afford **4g** (50 mg, 83%) as a white solid.

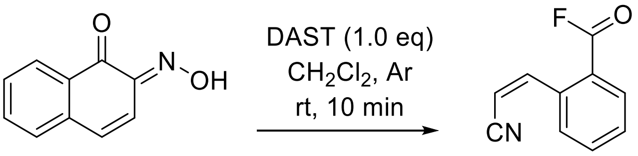
**8-cyano-1-naphthoyl fluoride (4g);** $R_f$ = 0.25 (Hex:EtOAc = 7:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.21-8.12 (m, 4H), 7.72-7.68 (m, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 46.13 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.0 (d, $J_{C,F}$ = 348 Hz), 137.3, 135.0, 134.4, 133.9,133.2, 128.4 (d, $J_{C,F}$ = 2 Hz), 126.5, 126.3, 124.0 (d, $J_{C,F}$ = 62 Hz), 117.3, 109.0. IR (neat) $\nu_{max}$ 2225, 1799, 1573, 1511, 1260 cm$^{-1}$. HRMS[EI+] calcd for $C_{12}H_6FNO$ $[M]^+$ 199.0433, found 199.0441.



**3h** **4h**

A 10 mL round bottom flask was charged with **3h** (52 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4h** (35 mg, 67%) as an orange oil.

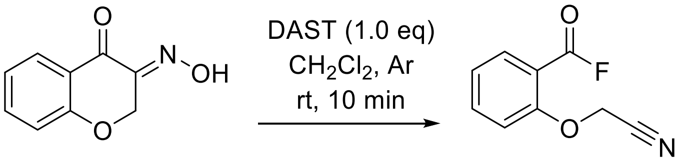
**(Z)-3-(2-cyanophenyl)acryloyl fluoride (4h);** $R_f$ = 0.3 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 2H), 7.66-7.62 (td, $J$ = 7.3 and 1.4 Hz, 1H), 7.58-7.49 (m, 2H), 6.20 (dd, $J$ = 12.2 and 1.6 Hz, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 43.07 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.6 (d, $J_{C,F}$ = 340 Hz), 146.5 (d, $J_{C,F}$ = 2 Hz), 137.0, 132.9, 132.7, 130.1, 129.8 (d, $J_{C,F}$ = 2 Hz), 118.2 (d, $J_{C,F}$ = 72 Hz), 117.1, 112.4. IR (neat) $\nu_{max}$ 2227, 1815, 1635, 1480, 1097 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_6FNO$ $[M]^+$ 175.0433, found 175.0422.



**3i** **4i**

A 10 mL round bottom flask was charged with **3i** (52 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4i** (39 mg, 74%) as a white solid.

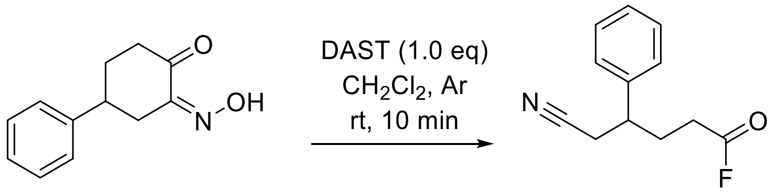
**(Z)-2-(2-cyanovinyl)benzoyl fluoride (4i);** $R_f$ = 0.3 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, $J$ = 7.8 and 1.4 Hz, 1H), 7.93-7.89 (m, 2H), 7.80 (td, $J$ = 7.6 and 1.4 Hz, 1H), 7.63-7.59 (td, $J$ = 7.7 and 1.2 Hz, 1H), 5.70 (d, $J$ = 11.8 Hz, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 27.66 (s, 1F) $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.9 (d, $J_{C,F}$ = 343 Hz), 148.1, 137.7 (d, $J_{C,F}$ = 7 Hz), 135.5, 132.8 (d, $J_{C,F}$ = 1 Hz). 130.5, 130.2 (d, $J_{C,F}$ = 3 Hz), 123.1 (d, $J_{C,F}$ = 58 Hz), 116.2, 100.1, IR (neat) $\nu_{max}$ 2219, 1804, 1567, 1483, 1303 cm$^{-1}$.HRMS[EI+] calcd for $C_{10}H_6FNO$ $[M]^+$ 175.0433, found 175.0438.



**3j** **4j**

A 10 mL round bottom flask was charged with **3j** (53 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **4j** (44 mg, 81%) as a light yellow solid.

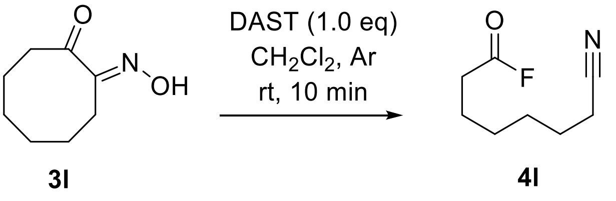
**2-(cyanomethoxy)benzoyl fluoride (4j)**; $R_f$ = 0.35 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, $J$ = 7.8 Hz, 1H), 7.74 (t, $J$ = 7.5 Hz, 1H), 7.28 (m, 1H), 7.20 (d, $J$ = 8.4 Hz, 1H), 4.95 (s, 2H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 32.61 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, $J_{C,F}$ = 4 Hz), 154.3 (d, $J_{C,F}$ = 342 Hz), 136.9, 134.3 (d, $J_{C,F}$ = 3 Hz), 123.6, 115.4 (d, $J_{C,F}$ = 61 Hz), 114.8 (d, $J_{C,F}$ = 3 Hz), 114.4, 54.5. IR (neat) $\nu_{max}$ 3015, 2245, 1812, 1790, 1597, 1488 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_6FNO_2$ $[M]^+$ 179.0383, found 179.0369.



**3k** **4k**

A 10 mL round bottom flask was charged with **3k** (61 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 7:1 to 3:1) to afford **4k** (47 mg, 77%) as a light brown oil.

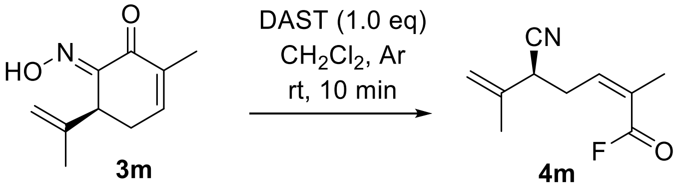
**5-cyano-4-phenylpentanoyl fluoride (4k);** $R_f$ = 0.25 (Hex:EtOAc = 7:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (m, 3H), 7.22-7.20 (m, 2H), 3.05 (m, 1H), 2.66-2.64 (m, 2H), 2.43-2.35 (m, 2H), 2.27 (m, 1H), 2.08 (m, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 45.82 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $J_{C,F}$ = 357 Hz), 139.5, 129.4, 128.3, 127.2, 117.9, 41.1, 29.9 (d, $J_{C,F}$ = 52 Hz), 29.03 (d, $J_{C,F}$ = 3 Hz), 25.3. IR (neat) $\nu_{max}$ 2926, 2263, 1832, 1451, 1087cm$^{-1}$. HRMS[FAB] calcd for $C_{12}H_{13}FNO$ $[M+H]^+$ 206.0981, found 206.1001.



**3l** **4l**

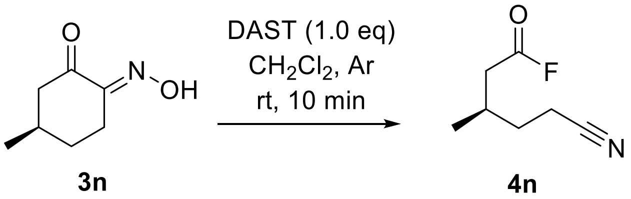
A 10 mL round bottom flask was charged with **3l** (47 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 2:1) to afford **4l** (38 mg, 81%) as a light yellow oil.

**5-cyano-2-phenylpentanoyl fluoride (4l)**; $R_f$ = 0.4 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.53 (t, $J$ = 7.3 Hz, 2H), 2.35 (t, $J$ = 7.1 Hz, 2H), 1.71-1.65 (m, 4H), 1.51-1.40 (m, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 45.60 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, $J_{C,F}$ = 358 Hz), 119.6, 32.0 (d, $J_{C,F}$ = 50 Hz), 28.3, 28.0, 25.2, 23.7 (d, $J_{C,F}$ = 2 Hz), 17.2. IR (neat) $\nu_{max}$ 2935, 2238, 1834, 1464, 1069 cm$^{-1}$. HRMS[FAB] calcd for $C_8H_{13}FNO$ $[M+H]^+$ 158.0981, found 158.0960.



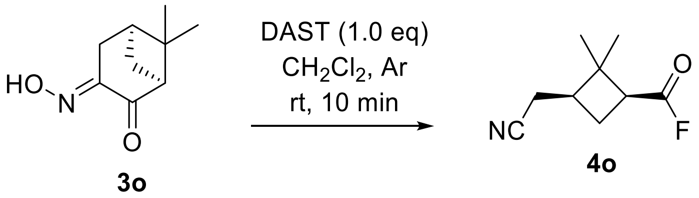
A 10 mL round bottom flask was charged with **3m** (54 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 7:1) to afford **4m** (34 mg, 63%) as a light yellow oil.

**(R,Z)-5-cyano-2,6-dimethylhepta-2,6-dienoyl fluoride (4m)**; $R_f = 0.4$ (Hex:EtOAc = 10:1); $^1H$ NMR (500 MHz, $CDCl_3$) δ 6.34 (m, 1H), 5.13 (m, 1H), 5.06 (m, 1H), 3.33 (m, 1H), 3.03-2.88 (m, 2H), 2.01-2.00 (m, 3H), 1.84 (s, 3H).$^{19}F$ NMR (376 MHz, $CDCl_3$) δ 38.08 (s, 1F). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 156.6 (d, $J_{C,F} = 347$ Hz), 144.6 (d, $J_{C,F} = 6$ Hz), 137.8, 126.2 (d, $J_{C,F} = 58$ Hz), 119.4, 115.9, 38.3, 31.2 (d, $J_{C,F} = 3$ Hz), 20.0, 19.9. IR (neat) $\nu_{max}$ 2982, 2243, 1804, 1650, 1456, 1072 $cm^{-1}$. HRMS[FAB] calcd for $C_{10}H_{13}FNO$ $[M+H]^+$ 182.0981, found 182.0979.



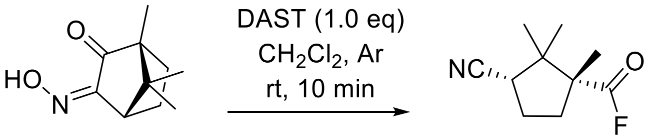
A 10 mL round bottom flask was charged with **3n** (42 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane:dther = 7:1 to 5:1) to afford **4n** (27 mg, 62%) as a colorless oil.

**(R)-5-cyano-3-methylpentanoyl fluoride (4n);** (rr = 10:1); $R_f = 0.35$ (Hex:EtOAc = 10:1); $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.54 (m, 1H), 2.46-2.34 (m, 3H), 2.15 (m, 1H), 1.83 (m, 1H), 1.61 (m, 1H), 1.08 (d, $J = 6.9$ Hz, 3H). $^{19}F$ NMR (376 MHz, $CDCl_3$) δ 48.65 (s, 1F). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.0 (d, $J_{C,F} = 359$ Hz), 119.1, 38.8 (d, $J_{C,F} = 49$ Hz), 31.4 (d, $J_{C,F} = 2$ Hz), 28.9 (d, $J_{C,F} = 2$ Hz), 18.6, 15.1. IR (neat) $\nu_{max}$ 2966, 2935, 2248, 1840, 1710, 1425 $cm^{-1}$. HRMS[EI+] calcd for $C_7H_{10}FNO$ $[M]^+$ 143.0746, found 143.0758.



A 10 mL round bottom flask was charged with **3o** (50 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 7:1 to 5:1) to afford **4o** (43 mg, 85%) as a light yellow oil.

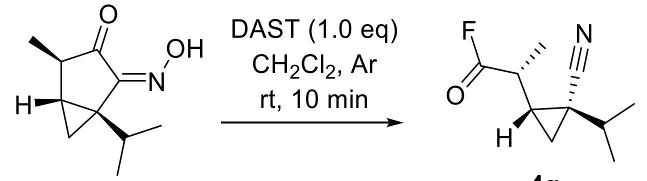
**(1S,3S)-3-(cyanomethyl)-2,2-dimethylcyclobutane-1-carbonyl fluoride (4o);** $R_f$ = 0.4 (Hex:EtOAc = 7:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.82 (m, 1H), 2.35-2.31 (m, 3H), 2.20 (m, 1H), 1.97 (m, 1H), 1.32 (s, 3H), 1.08 (s, 3H), $^{19}$F NMR (376 MHz, $CDCl_3$) δ 42.92 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, $J_{C,F}$ = 358 Hz), 118.0, 44.5 (d, $J_{C,F}$ = 52 Hz), 43.4 (d, $J_{C,F}$ = 2 Hz), 38.5 (d, $J_{C,F}$ = 3 Hz), 29.7, 24.4 (d, $J_{C,F}$ = 4 Hz), 17.8 (d, $J_{C,F}$ = 2 Hz), 17.7. IR (neat) $\nu_{max}$ 2959, 2245, 1828, 1371, 1238 cm$^{-1}$. HRMS[FAB] calcd for $C_9H_{13}FNO$ $[M+H]^+$ 170.0981, found 170.0981.



**3p** **4p**

A 10 mL round bottom flask was charged with **3p** (54 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 3:1) to afford **4p** (51 mg, 93%) as a light yellow oil.

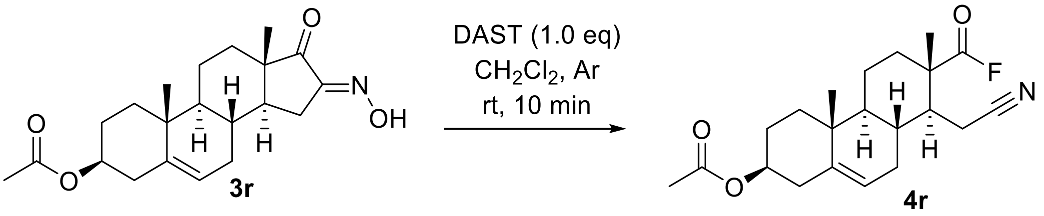
**(1R,3S)-3-cyano-1,2,2-trimethylcyclopentane-1-carbonyl fluoride (4p);** $R_f$ = 0.6 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.83 (t, $J$ = 9.9 Hz, 1H), 2.62 (m, 1H), 2.18 (m, 1H), 2.06 (m, 1H), 1.72 (m, 1H), 1.29 (s, 3H), 1.26 (s, 3H), 1.19 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 35.77 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.9 (d, $J_{C,F}$ = 369 Hz), 119.9, 54.6 (d, $J_{C,F}$ = 44 Hz), 46.7 (d, $J_{C,F}$ = 3 Hz), 39.4 (d, $J_{C,F}$ = 5 Hz), 32.9 (d, $J_{C,F}$ = 2 Hz), 24.8, 22.0, 21.9 (d, $J_{C,F}$ = 3 Hz), 21.0. IR (neat) $\nu_{max}$ 2977, 2243, 1826, 1462, 1384, 1049 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_{14}FNO$ $[M]^+$ 183.1059, found 183.1075.



**3q** **4q**

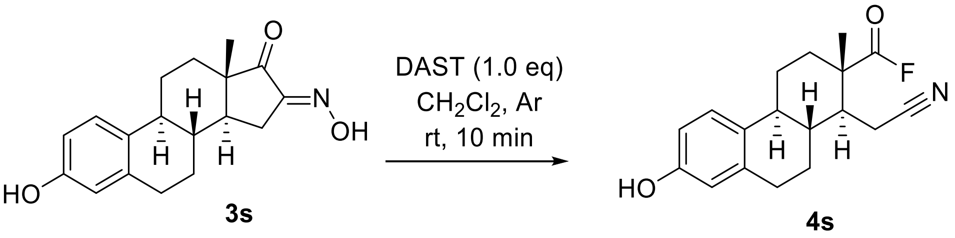
A 10 mL round bottom flask was charged with **3q** (54 mg, .3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 μL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford **4q** (40 mg, 72%) as a colorless oil.

**(R)-2-((1R,2S)-2-cyano-2-isopropylcyclopropyl) propanoyl fluoride (4q) ;** $R_f$ = 0.4 (Hex:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 2.39 (m, 1H), 1.44 (d, $J$ = 7.2 Hz, 3H), 1.38-1.25 (m, 2H), 1.17 (d, $J$ = 5.2 Hz, 3H), 1.14-1.12 (m, 3H), 1.05 (m, 1H), 0.97 (t, $J$ = 6.4 Hz, 1H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 38.44 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, $J_{C,F}$ = 365 Hz), 199.8, 40.4 (d, $J_{C,F}$ = 50 Hz), 35.0, 27.1 (d, $J_{C,F}$ = 1 Hz), 24.4, 20.0, 19.7, 18.3, 16.2. IR (neat) $\nu_{max}$ 2965, 2228, 1834, 1739, 1459, 1045 cm$^{-1}$. HRMS[EI+] calcd for $C_{10}H_{14}FNO$ $[M]^+$ 183.1059, found 183.1059.



A 10 mL round bottom flask was charged with **3r** (108 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 7:1 to 3:1) to afford **4r** (64 mg, 59%) as a white solid.

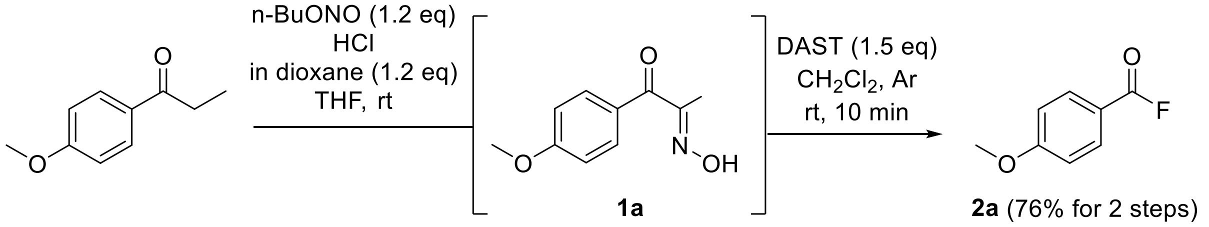
**(2S,4aR,4bS,7S,8S,8aR)-8-(cyanomethyl)-7-(fluorocarbonyl)-4a,7-dimethyl-1,2,3,4,4a,4b,5,6,7,8,8a,9-dodecahydrophenanthren-2-yl acetate (4r) ;** $R_f$ = 0.6 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 5.39 (m, 1H), 4.60 (m, 1H), 2.60 (dd, *J* = 17.8 and 6.0 Hz, 1H), 2.40-2.25 (m, 4H), 2.03 (s, 3H), 1.99-1.85 (m, 4H), 1.82-1.69 (m, 4H), 1.38 (s, 3H), 1.58 (m, 1H), 1.47 (m, 1H), 1.21-1.11 (m, 2H), 1.04 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 27.31 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.6, 167.0 (d, $J_{C,F}$ = 372 Hz), 139.5, 121.0, 118.0, 73.5, 48.5, 47.0 (d, $J_{C,F}$ = 40 Hz), 43.0, 37.8, 36.8, 36.7, 35.76, 35.74, 31.4, 31.3, 27.6, 21.5, 19.2 (d, $J_{C,F}$ = 1 Hz), 18.2, 15.2. IR (neat) $\nu_{max}$ 2948, 2247, 1821, 1730, 1635, 1251 cm$^{-1}$ . HRMS[FAB] calcd for $C_{21}H_{29}FNO_3$ $[M+H]^+$ 362.2131, found 362.2159.



A 10 mL round bottom flask was charged with **3s** (90 mg, 0.3 mmol) and dry $CH_2Cl_2$ (1.0 mL) under Ar. Then, (diethylamino)sulfur trifluoride (DAST, 40 µL, 0.3 mmol) was added to the solution via a microsyringe at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford **4s** (67 mg, 74%) as a white solid.

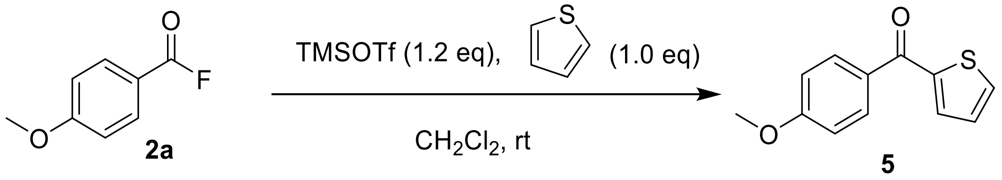
**(1S,2S,4aS,10aR)-1-(cyanomethyl)-7-hydroxy-2-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-2-carbonyl fluoride (4s) ;** $R_f$ = 0.3 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 1H), 6.65 (dd , *J* = 8.5 and 2.7 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 4.89 (s, 1H), 2.97-2.84 (m, 2H), 2.69 (dd, *J* = 17.8 and 5.9 Hz, 1H), 2.46-2.37 (m, 3H), 2.20 (m, 1H), 2.12 (m, 1H), 2.06-1.94 (m, 2H), 1.67 (m, 1H), 1.54-1.43 (m, 2H), 1.39 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ 27.55 (s, 1F). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.1 (d, $J_{C,F}$ = 372 Hz), 154.0, 137.6, 130.5, 126.6, 118.2, 115.3, 113.3, 47.4 (d, $J_{C,F}$ = 40 Hz), 42.4, 41.7, 38.7, 35.9 (d, $J_{C,F}$ = 1 Hz), 29.5, 26.7, 25.2, 18.5, 15.2. IR (neat) $\nu_{max}$ 3342, 2942, 2261, 1817, 1714, 1503 cm$^{-1}$. HRMS[EI+] calcd for $C_{18}H_{20}FNO_2$ $[M]^+$ 301.1478, found 301.1473.

### A procedure for one-pot reaction



To a stirred solution of ketone (328 mg, 2.0 mmol) and n-butyl nitrite (0.28 mL, 2.4 mmol) in THF (6.0 mL) was added 4N HCl in 1,4-dioxane (0.6 mL, 2.4 mmol) under Ar. After 3 h, (diethylamino)sulfur trifluoride (DAST, 0.4 mL, 3.0 mmol) was added to the solution at room temperature. After 10 min, the reaction mixture was diluted with diethyl ether (10 mL), washed with 1N HCl solution (5.0 mL) and subsequently with sat. $NaHCO_3$ sol'n. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (pentane) to afford **2a** (234 mg, 76%) as a pale yellow oil.

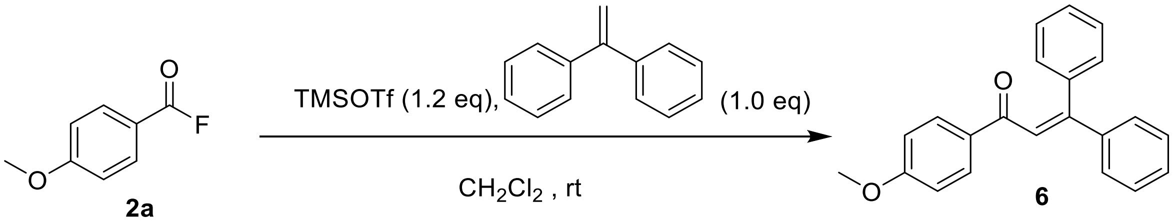
### Preparation of ketone 5



A 10 mL round bottom flask was filled with argon gas and charged with **2a** (154 mg, 1.0 mmol) and TMSOTf (215 µL, 1.2 mmol) in $CH_2Cl_2$ (2.0 mL) at room temperature. Then, a solution of thiophene (80 µL, 1.0 mmol) in $CH_2Cl_2$ (1.0 mL) was added to the reaction mixture. After for 30 min, the reaction mixture was concentrated under reduced pressure and directly subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford the ketone **5** (185 mg, 85%) as a white solid.

$R_f$ = 0.45 (Hex:EtOAc = 7:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.68 (dd, *J* = 5.0 and 1.2 Hz , 1H), 7.64 (dd, *J* = 4.9 and 3.8 Hz, 1H), 7.15 (m, 1H), 6.99-6.67 (m, 2H), 3.89 (s, 3H). This spectral data is in agreement with the reported.[16]

### Preparation of ketone 6



A 10 mL round bottom flask was filled with argon gas and charged with **2a** (154 mg, 1.0 mmol) and TMSOTf (215 µL, 1.2 mmol) in $CH_2Cl_2$ (2.0 mL) at room temperature. Then, a solution of 1,1-

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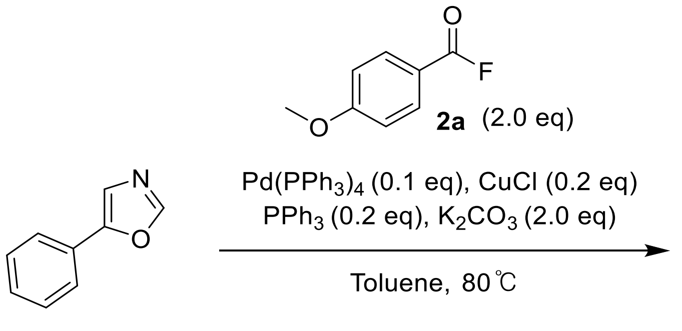
[16] Zhao, W.; Carreira, E. M. *Chem. Eur. J.* **2007**, *13*, 2671.

diphenylethylene (176 μL, 1.0 mmol) in $CH_2Cl_2$ (1.0 mL) was added to the reaction mixture. After 30 min, the reaction mixture was concentrated under reduced pressure and directly subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 5:1) to afford the ketone **6** (226 mg, 72%) as a white solid.

$R_f$ = 0.4 (Hex:EtOAc = 7:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.40-7.37 (m, 5H), 7.29-7.26 (m, 3H), 7.20-7.18 (m, 2H), 7.08 (s, 1H), 6.88-6.85 (m, 2H), 3.84 (s, 3H). This spectral data is in agreement with the reported.[17]

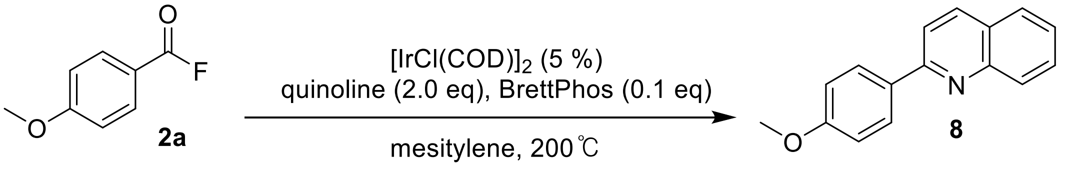
**Preparation of ketone 7**



A 7 mL vial was charged with $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), $PPh_3$ (26 mg, 0.1 mmol), CuCl (10 mg, 0.1 mmol), and $K_2CO_3$ (138 mg, 1.0 mmol) and it was flushed with argon gas. Then, a solution of **2a** (154 mg, 1.0 mmol) and 5-phenyloxazole (73 mg, 0.5 mmol) in toluene (2.0 mL) was added to the vial. The reaction mixture was heated at 80 °C in oil bath for 24h. After completion of the reaction, the reaction mixture was cooled down to room temperature, diluted with $H_2O$ (10 mL), and extracted with ethyl acetate (10 X 3 mL). The organic solution was dried over anhydrous $MgSO_4$, concentrated, and the crude product was subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 3:1) to afford the ketone **7** (106 mg, 76%) as white solid.

$R_f$ = 0.45 (Hex:EtOAc = 6:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, $J$ = 8.5 Hz , 2H), 7.82 (d, $J$ = 7.5 Hz , 2H), 7.59 (s, 1H), 7.49-7.39 (m, 3H), 7.01(d, $J$ = 8.5 Hz , 2H), 3.90 (s, 3H). This spectral data is in agreement with the reported.[18]

**Preparation of 2-arylquinoline 8**



A 7 mL vial was charged with $[IrCl(COD)]_2$ (33 mg, 0.05 mmol), BrettPhos (53 mg, 0.1 mmol), quinolone (236 μL, 2.0 mmol), and mesitylene (3.0 mL) under Ar. To the stirred mixture was added a solution of **2a** (154 mg, 1.0 mmol) in mesitylene (1.0 mL). The mixture was heated at 200 °C for 16 h in heating mantle. Then, the reaction mixture was cooled down to room temperature, filtered through a short pad of silica gel and eluted with EtOAc. The filtrate was concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 20:1 to 10:1) to afford the 2-arylquinoline **8** (132 mg, 56%) as a white solid.

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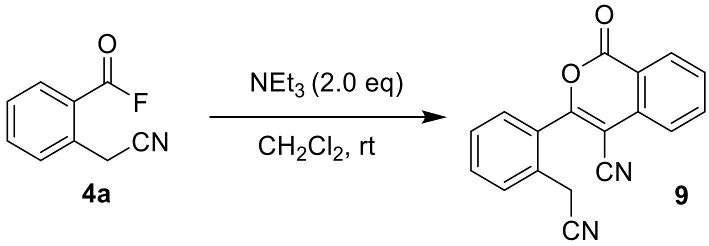
[17] Liu, Y.; Chen, Z.; Wang, Q. L.; Chen, P.; Xie, J.; Xiong, B. Q.; Zhang, P. L.; Tang, K. W. *J. Org. Chem.* **2020**, *85*, 2385.

[18] Wu, X. F.; Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 7316.

$R_f$ = 0.4 (Hex:EtOAc = 20:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18-8.12 (m, 4H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.79 (m, 1H), 7.70 (m, 1H), 7.50 (m, 1H), 7.06-7.04 (m, 2H), 3.88 (s, 3H). This spectral data is in agreement with the reported.[19]

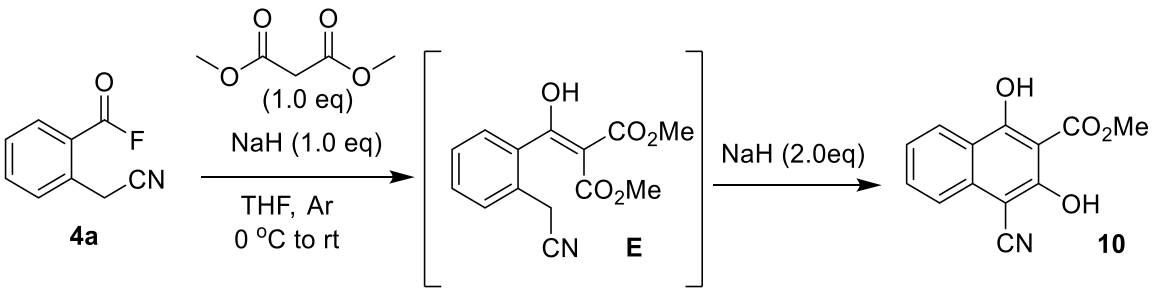
**Preparation of isocoumarin 9**



To a stirred solution of **4a** (163 mg, 1.0 mmol) in $CH_2Cl_2$ (3.0 mL) was added trimethylamine (279 µL, 2.0 mmol) at room temperature. After 1h, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with $H_2O$. The organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 3:1) to afford the isocoumarin **9** (209 mg, 73%) as a white solid.

$R_f$ = 0.4 (Hex:EtOAc = 3:1); $^1$H NMR (500 MHz, $CDCl_3$) δ 8.35 (m, 1H), 7.94 (m, 1H), 7.86 (m, 1H), 7.76 (m, 1H), 7.71 (m, 1H), 7.63-7.62 (m, 2H), 7.54 (m, 1H), 4.98 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.7, 158.9, 136.4, 133.3, 132.7, 131.1, 130.7, 130.4, 130.2, 129.67, 129.62, 128.9, 124.8, 119.0, 116.7, 113.9, 94.9, 22.5. IR (neat) $\nu_{max}$ 2227, 1763, 1615, 1489, 1237, 1033 cm$^{-1}$. HRMS[EI+] calcd for $C_{18}H_{10}N_2O_2$ $[M]^+$ 286.0742, found 286.0749.

**Preparation of 1,3-naphthalenediol 10**



To a stirred solution of dimethylmalonate (132 mg, 1.0 mmol) in dry THF (3.0 mL) was added NaH (60% dispersion in mineral oil, 40 mg, 1.0 mmol) at 0 °C under Ar. After stirring for 20 min, the acyl fluoride **4a** (163 mg, 1.0 mmol) in THF (1.0 mL) was slowly added to the reaction mixture. After being kept in the ice-bath for 1h, **4a** disappeared and formation of intermediate **E** was monitored by tlc. Subsequently, NaH (60% dispersion in mineral oil, 80 mg, 2.0 mmol) was added and the ice-bath was removed. Upon completion of the reaction (3 h), it was quenched with sat. $NH_4Cl$ sol'n and extracted with ethyl aceate (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1 to 1:1) to afford the naphthalenediol **10** (151 mg, 62%) as an off-white solid.

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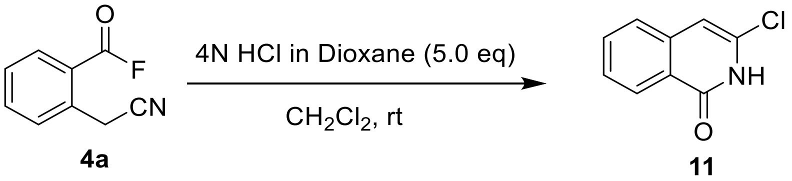
[19] Rahul, P.; Nitha, P. R.; Omanakuttan, V. K.; Babu, S. A.; P. Sasikumar.; Vakayil, K. P.; Henning, H.; Jubi, J. *Eur. J. Org. Chem*. **2020**, 3081.

R$_f$ = 0.5 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.13 (br s, 2H), 8.25 (d, $J$ = 8.2 Hz, 1H), 7.81-7.77 (m, 2H), 7.50 (m, 1H), 3.99 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 168.6, 162.2, 160.6, 134.5, 132.4, 124.74, 124.46, 122.8, 119.6, 115.8, 100.9, 85.0, 53.3. IR (neat) $\nu_{max}$ 3394, 2219, 1660, 1633, 1502, 1241 cm$^{-1}$. HRMS[EI+] calcd for $C_{13}H_9NO_4$ [M]$^+$ 243.0532, found 243.0541.

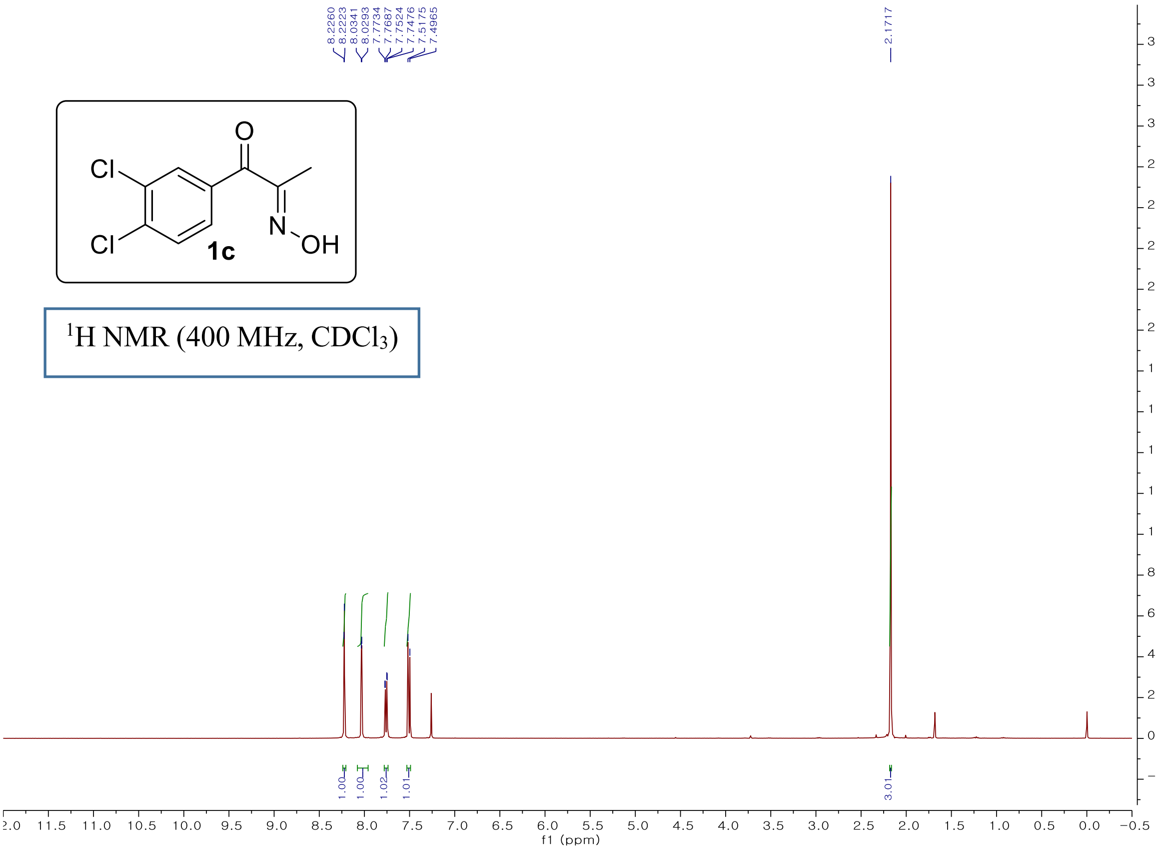
**Preparation of isoquinolone 11**



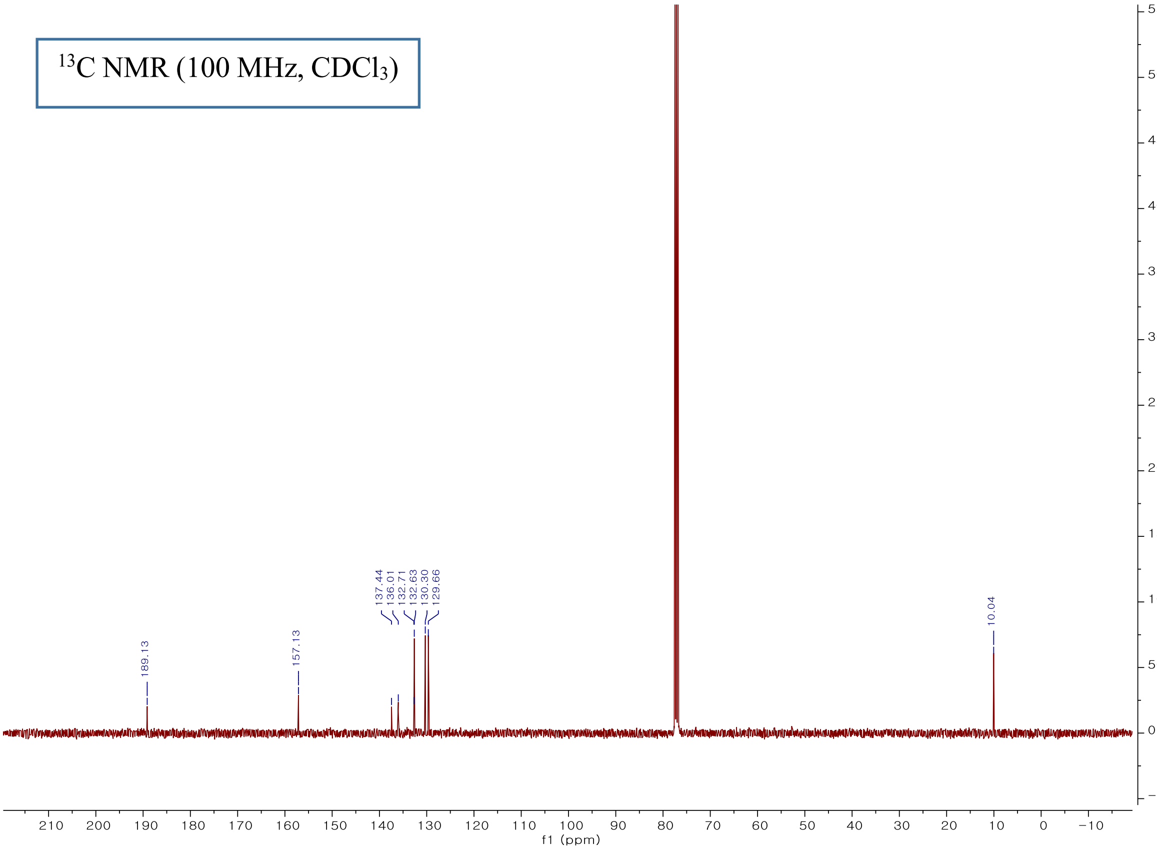
To a stirred solution of **4a** (163 mg, 1.0 mmol) in $CH_2Cl_2$ (3.0 mL) was added 4N HCl in Dioxane (1.25 mL, 5.0 mmol) at room temperature under Ar. After 2 days, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n, extracted with ethyl acetate (10 X 3 mL). The combined organic solution was dried over $MgSO_4$, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1 to 3:1) to afford the isoquinolone **11** (98 mg, 55%) as a white solid.

R$_f$ = 0.4 (Hex:EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) δ 11.12 (br s, 1H), 8.40 (d, $J$ = 7.6 Hz, 1H), 7.67 (m, 1H), 7.49 (t, $J$ = 7.8 Hz, 2H), 6.58 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.1, 138.0, 133.5, 128.6, 127.9, 127.1, 125.8, 124.4, 105.5. IR (neat) $\nu_{max}$ 2817, 1651, 1625, 1442, 1338, 1148 cm$^{-1}$. HRMS[EI+] calcd for $C_9H_6ClNO$ [M]$^+$ 179.0138, found 179.0141.

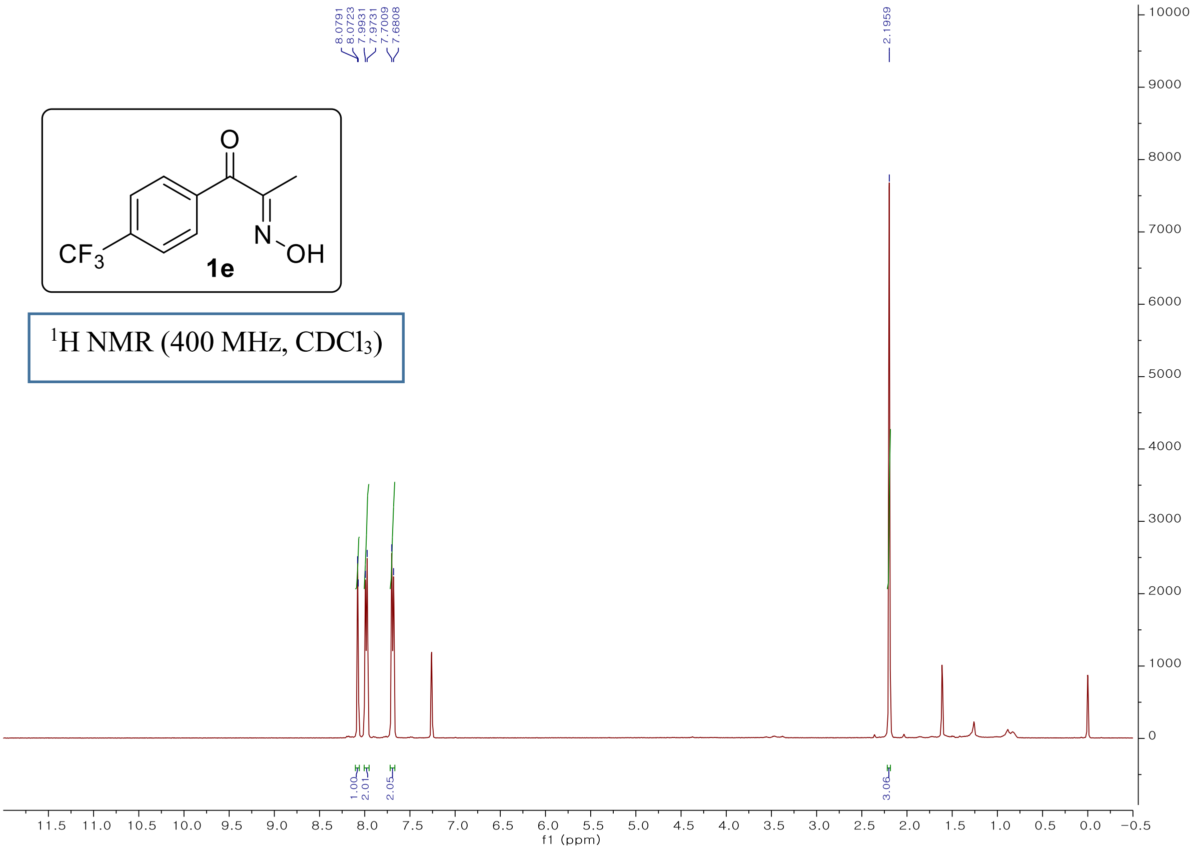
## $^1$H-NMR, $^{13}$C-NMR, $^{19}$F-NMR



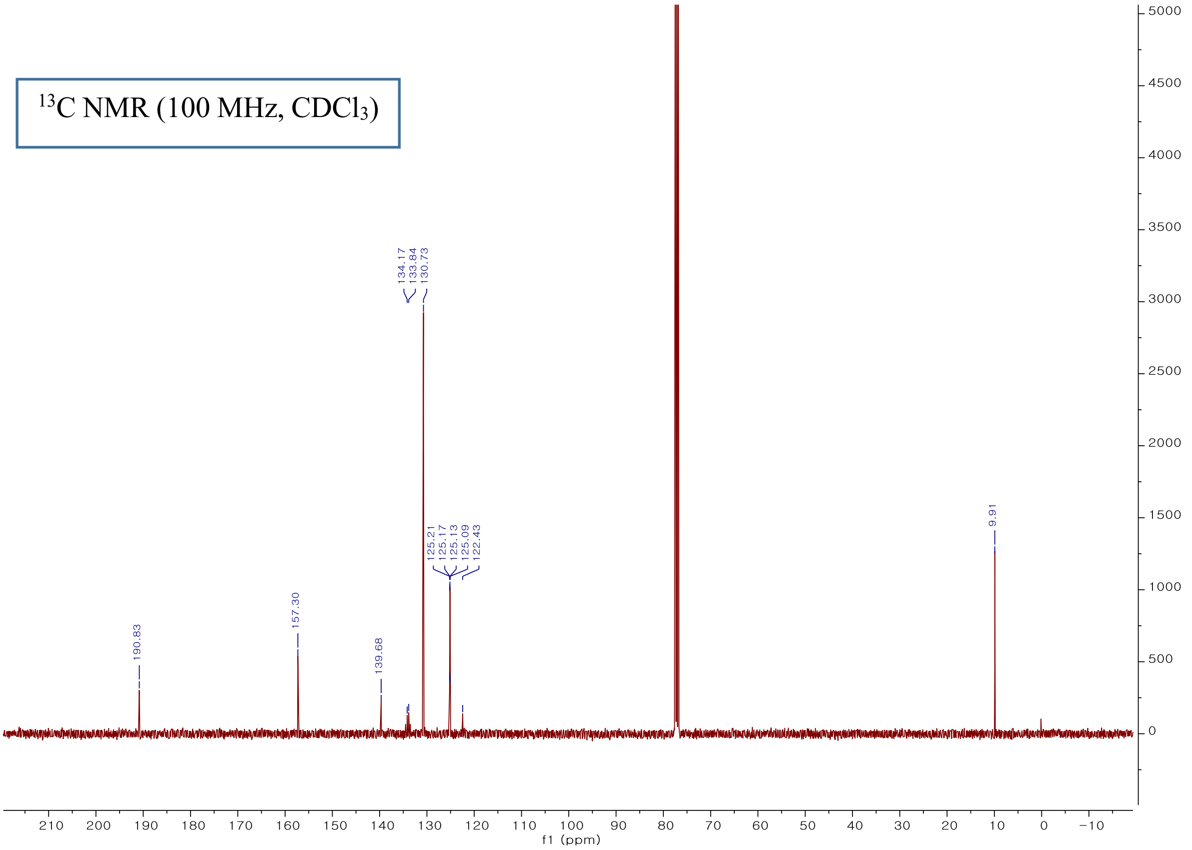
$^1$H NMR (400 MHz, $CDCl_3$)



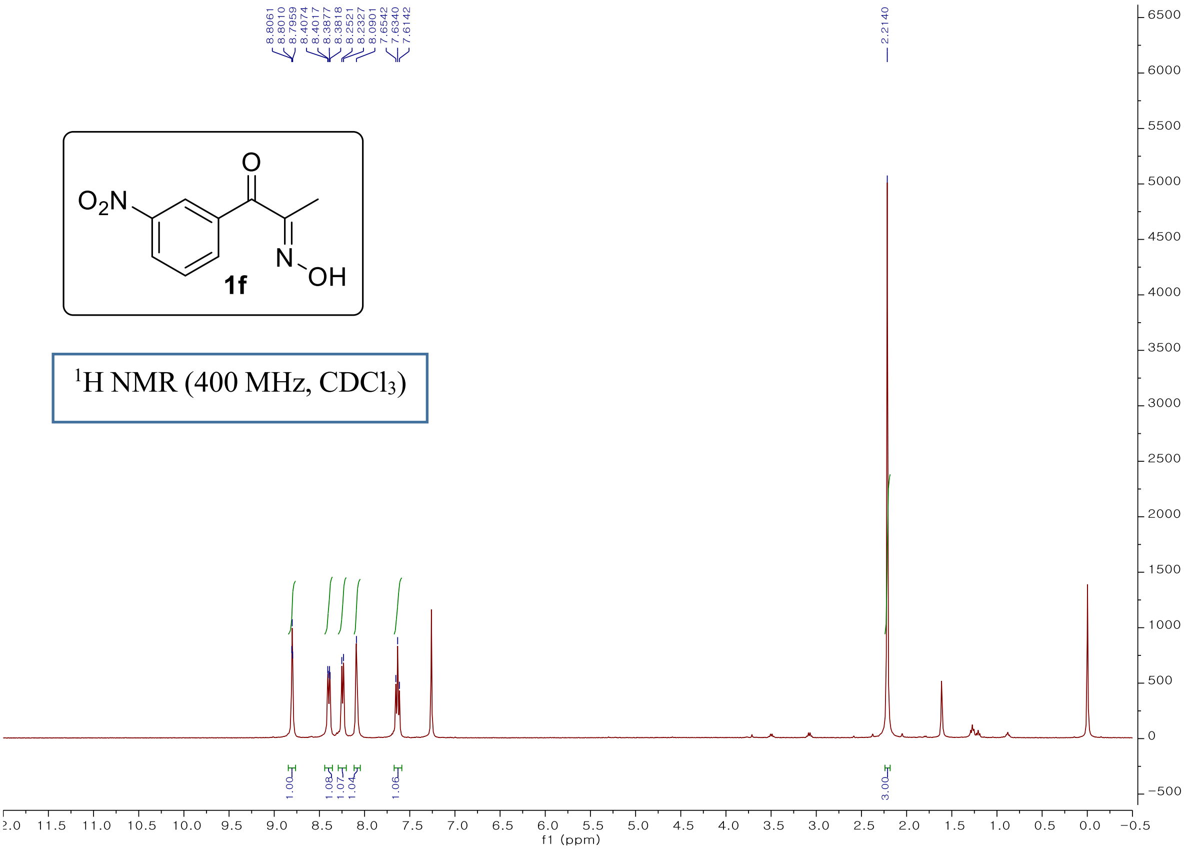
$^{13}$C NMR (100 MHz, $CDCl_3$)



$^1$H NMR (400 MHz, $CDCl_3$)

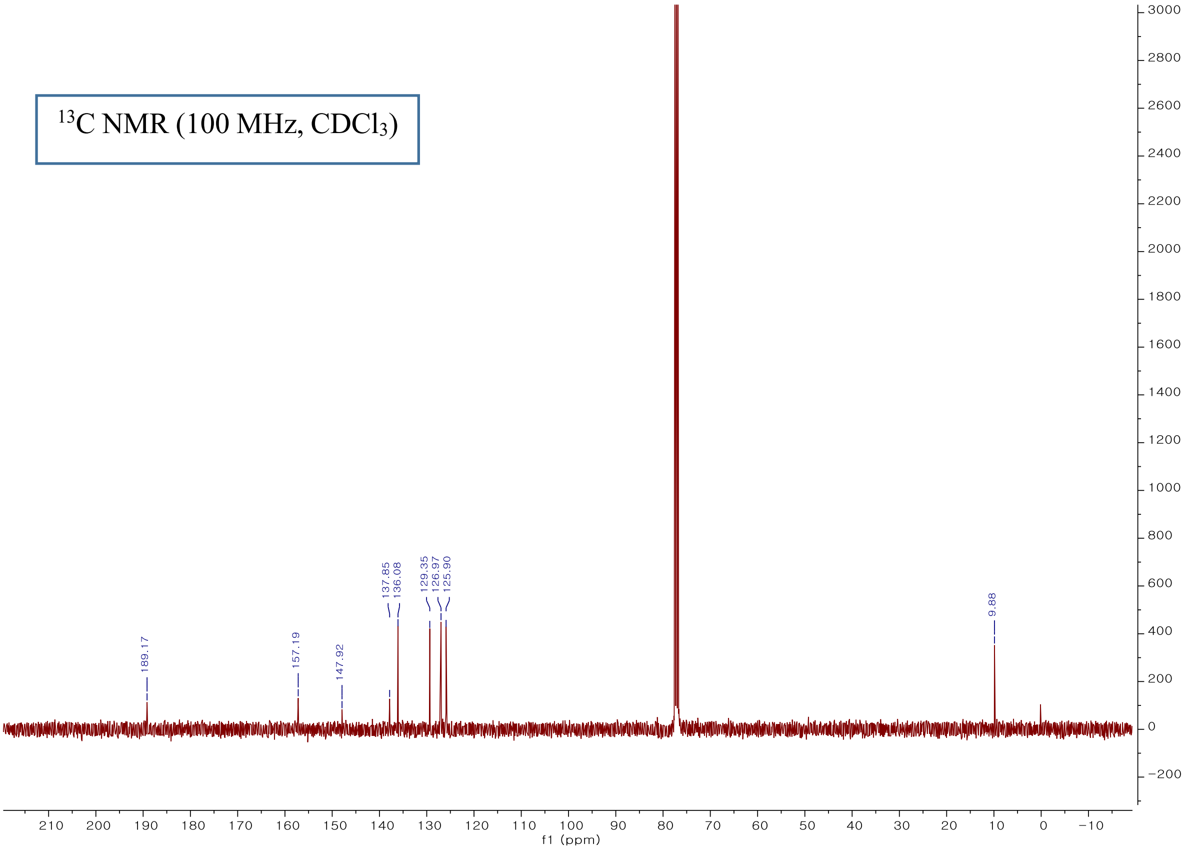


$^{13}$C NMR (100 MHz, $CDCl_3$)

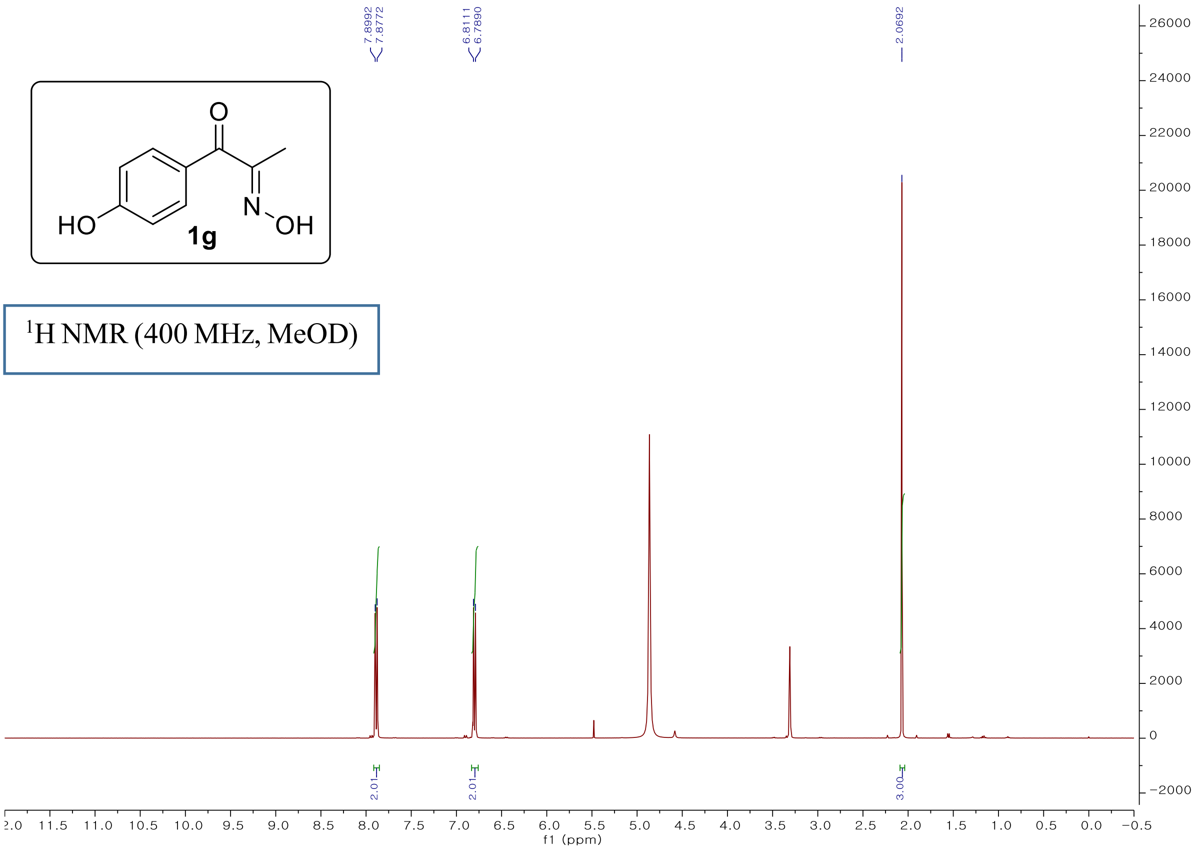


1f

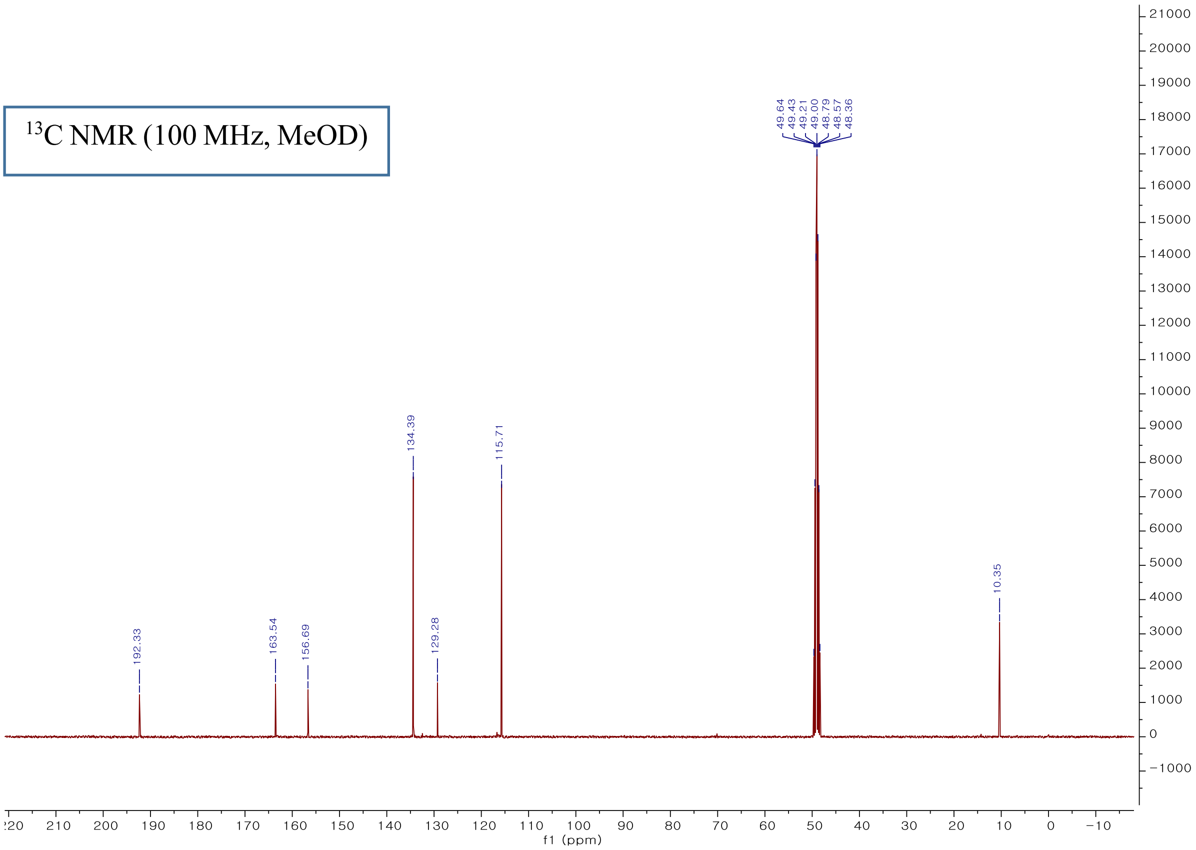
$^1$H NMR (400 MHz, CDCl$_3$)



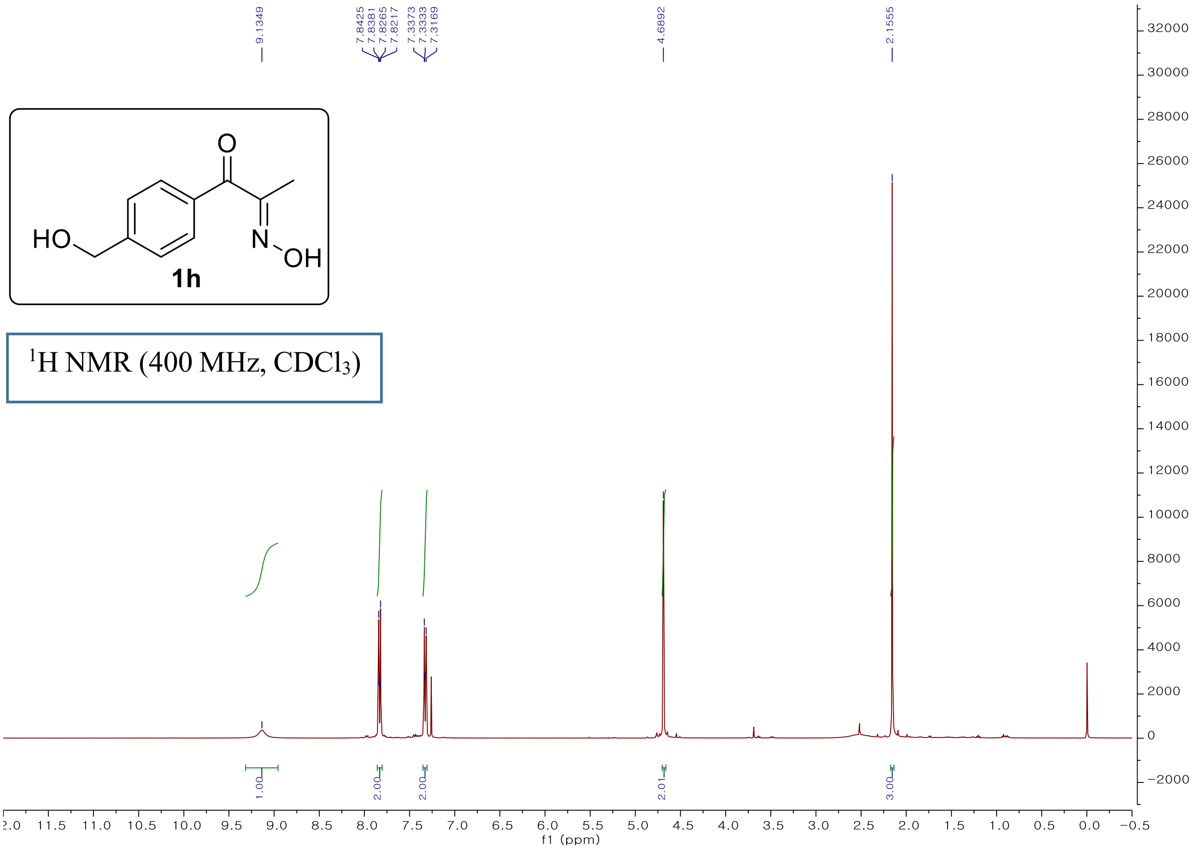
$^{13}$C NMR (100 MHz, CDCl$_3$)



$^1$H NMR (400 MHz, MeOD)

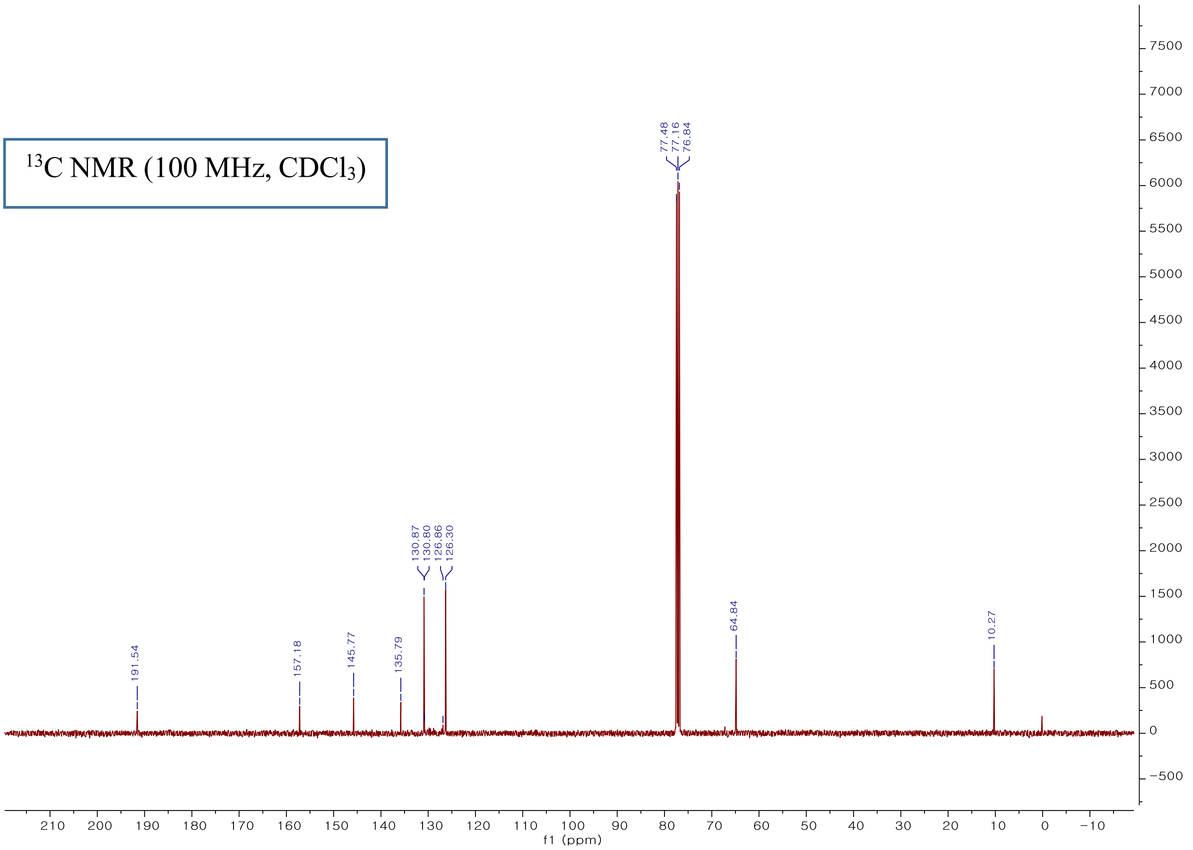


$^{13}$C NMR (100 MHz, MeOD)

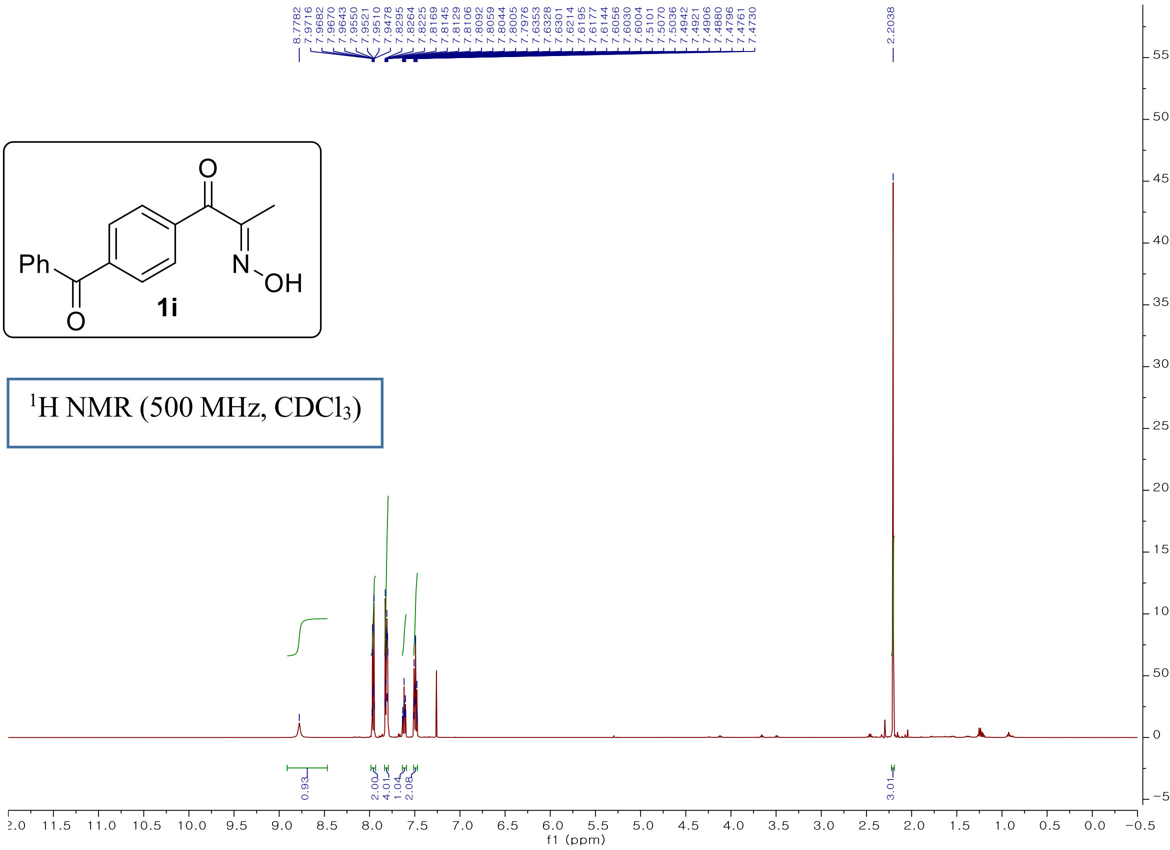


**1h**

$^1$H NMR (400 MHz, CDCl$_3$)

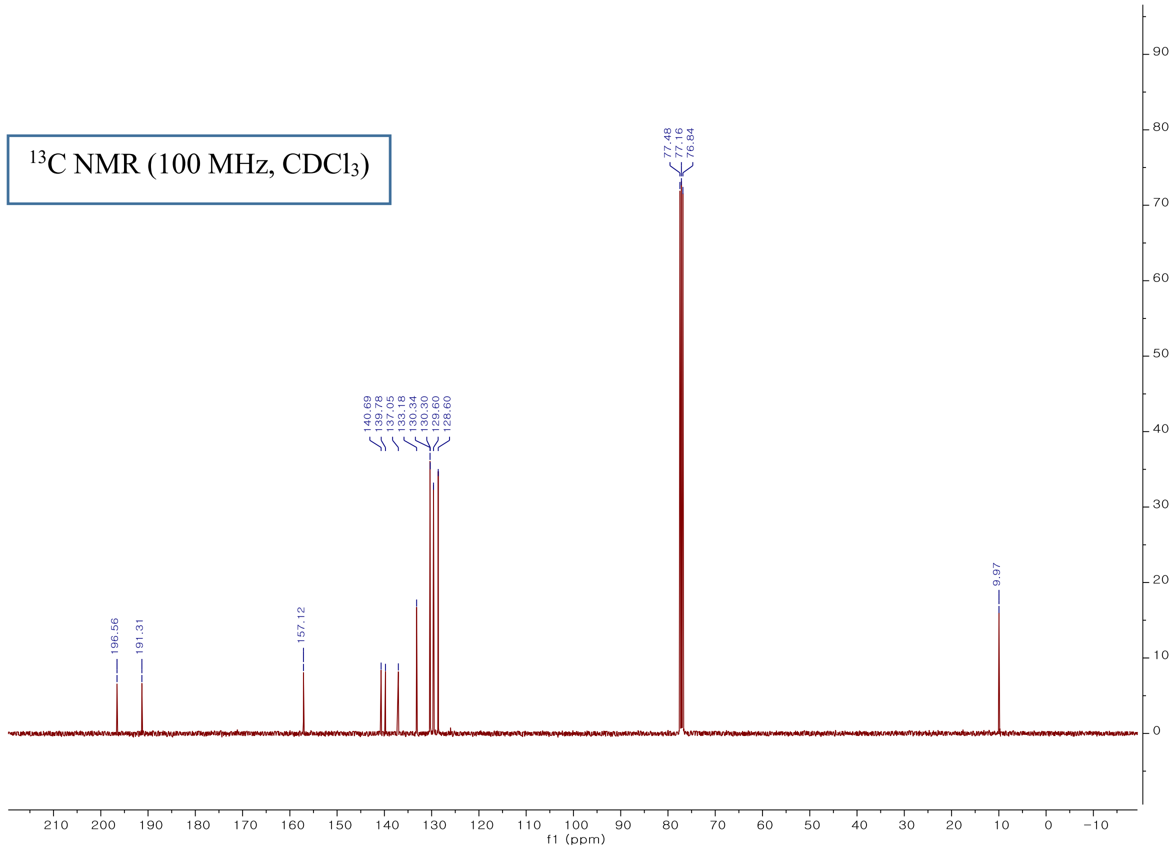


$^{13}$C NMR (100 MHz, CDCl$_3$)

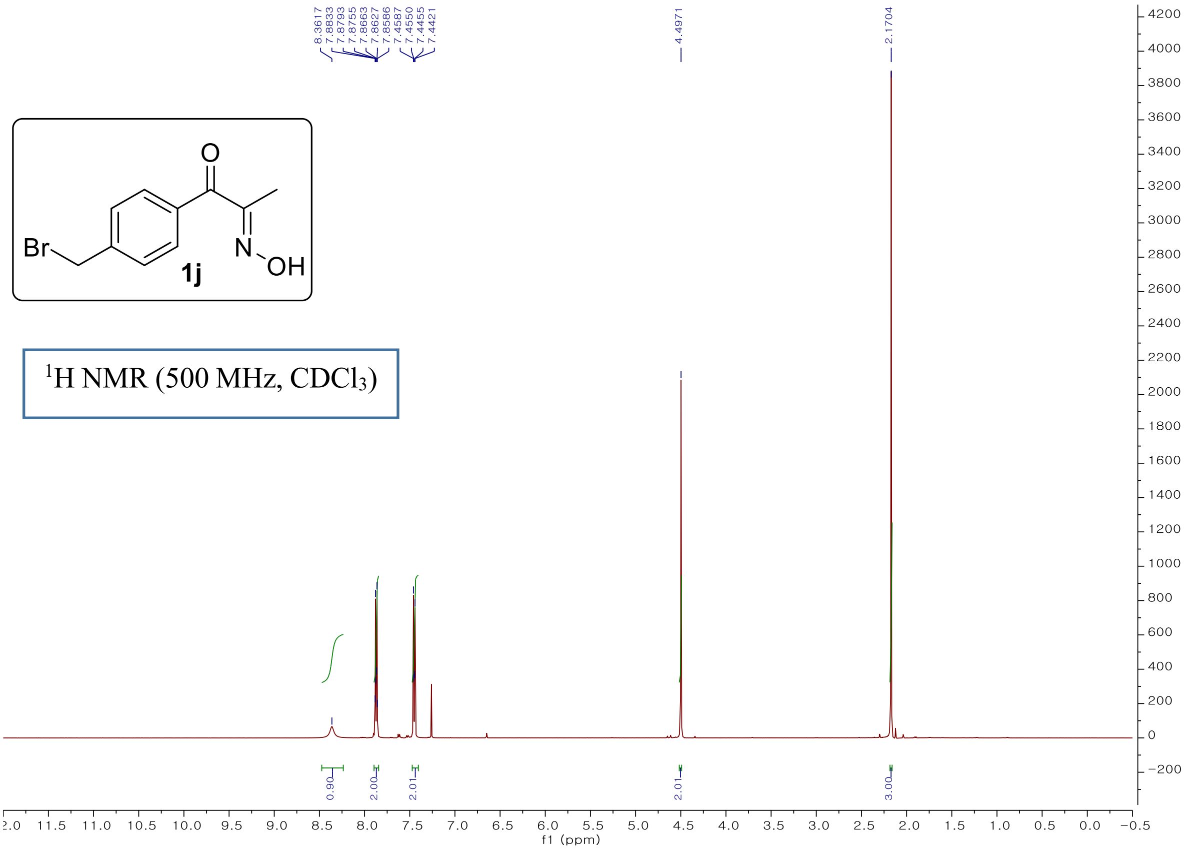


**1i**

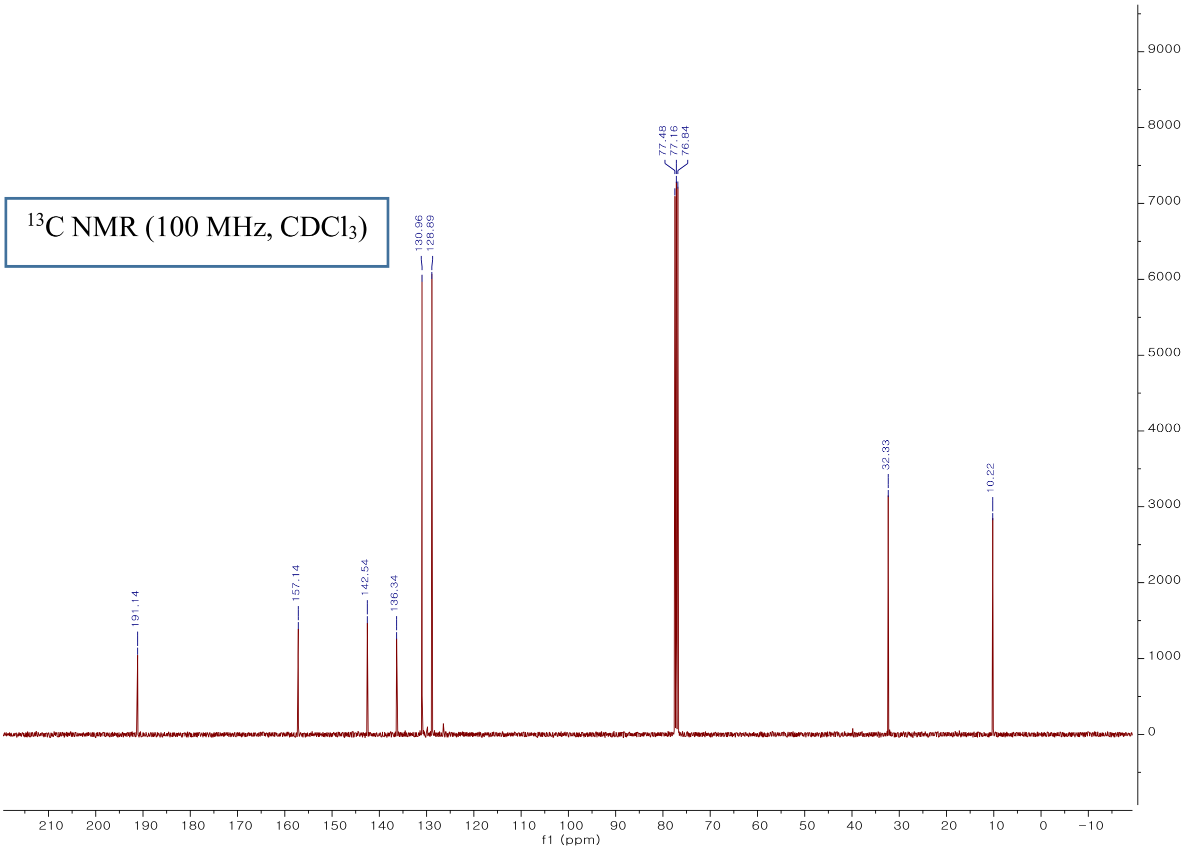
$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)

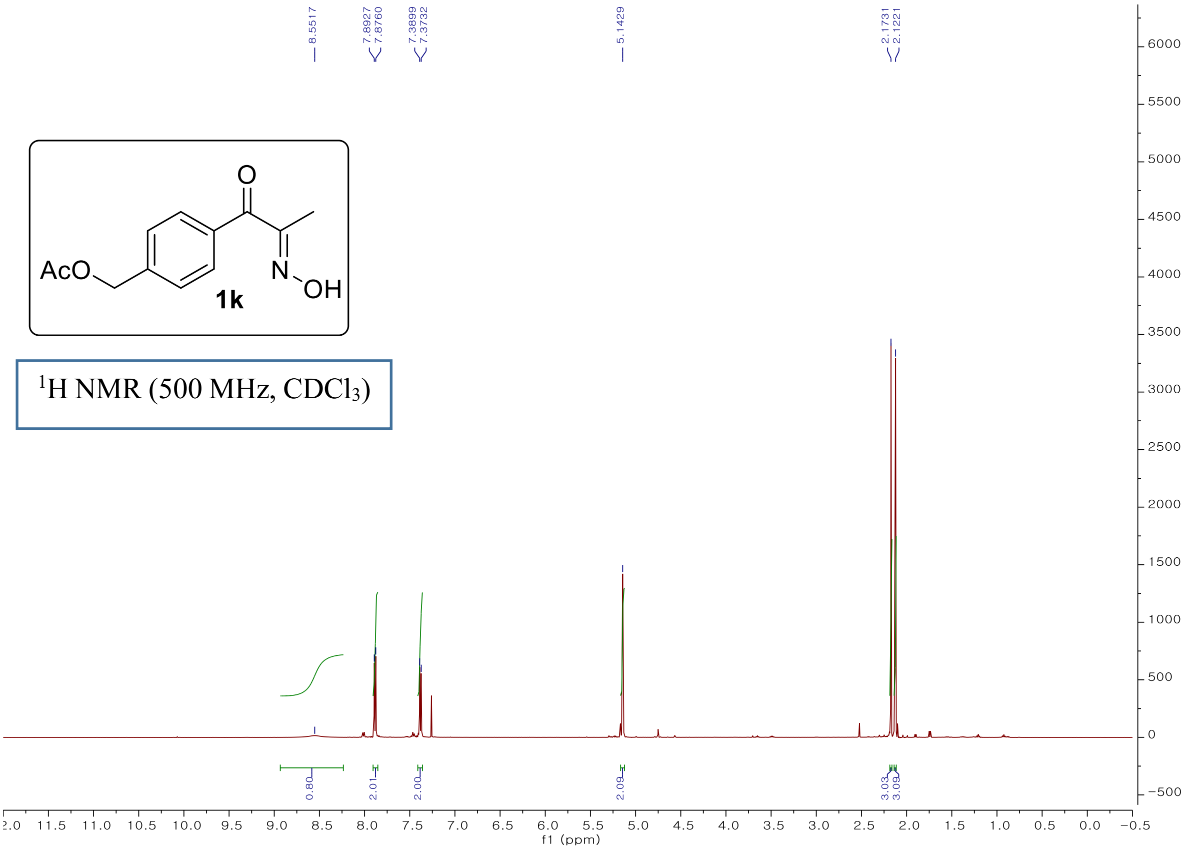


¹H NMR (500 MHz, $CDCl_3$)



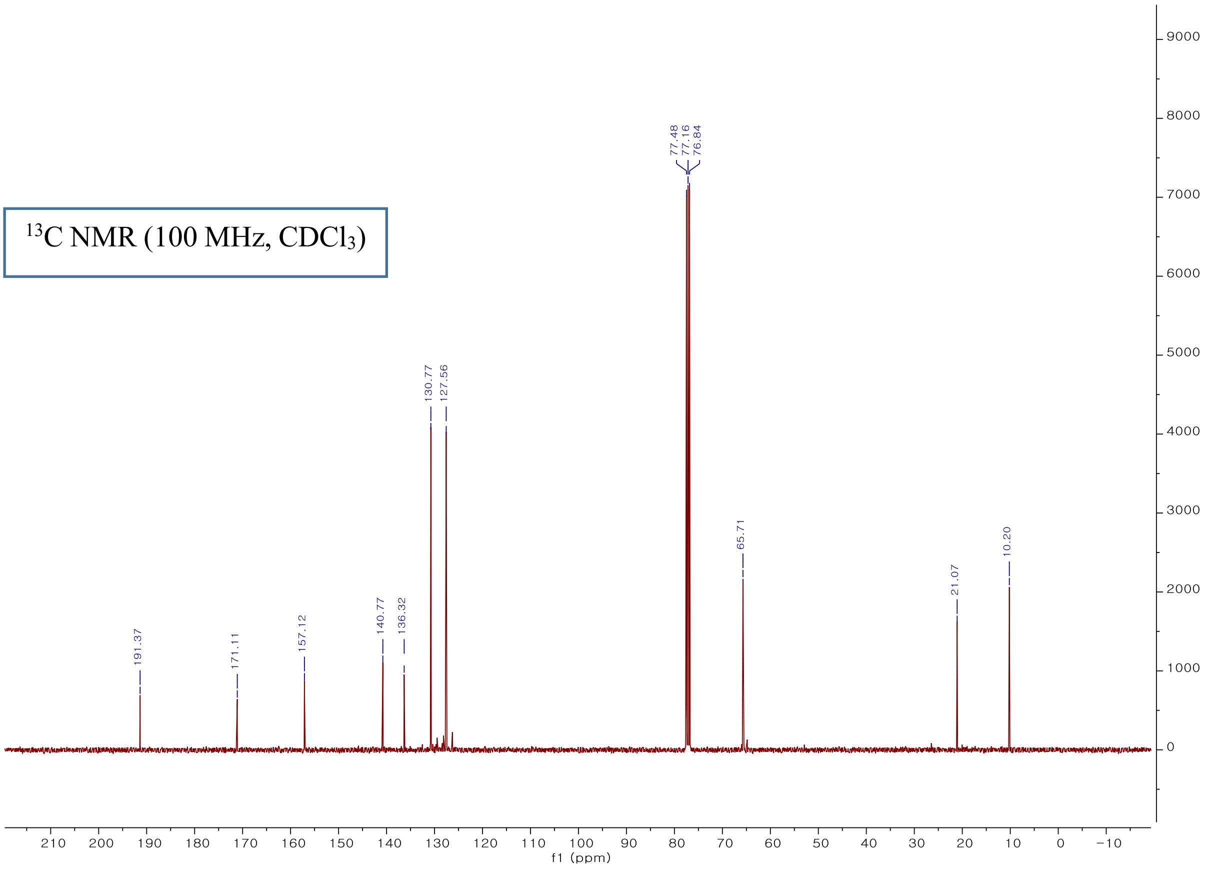
¹³C NMR (100 MHz, $CDCl_3$)

,

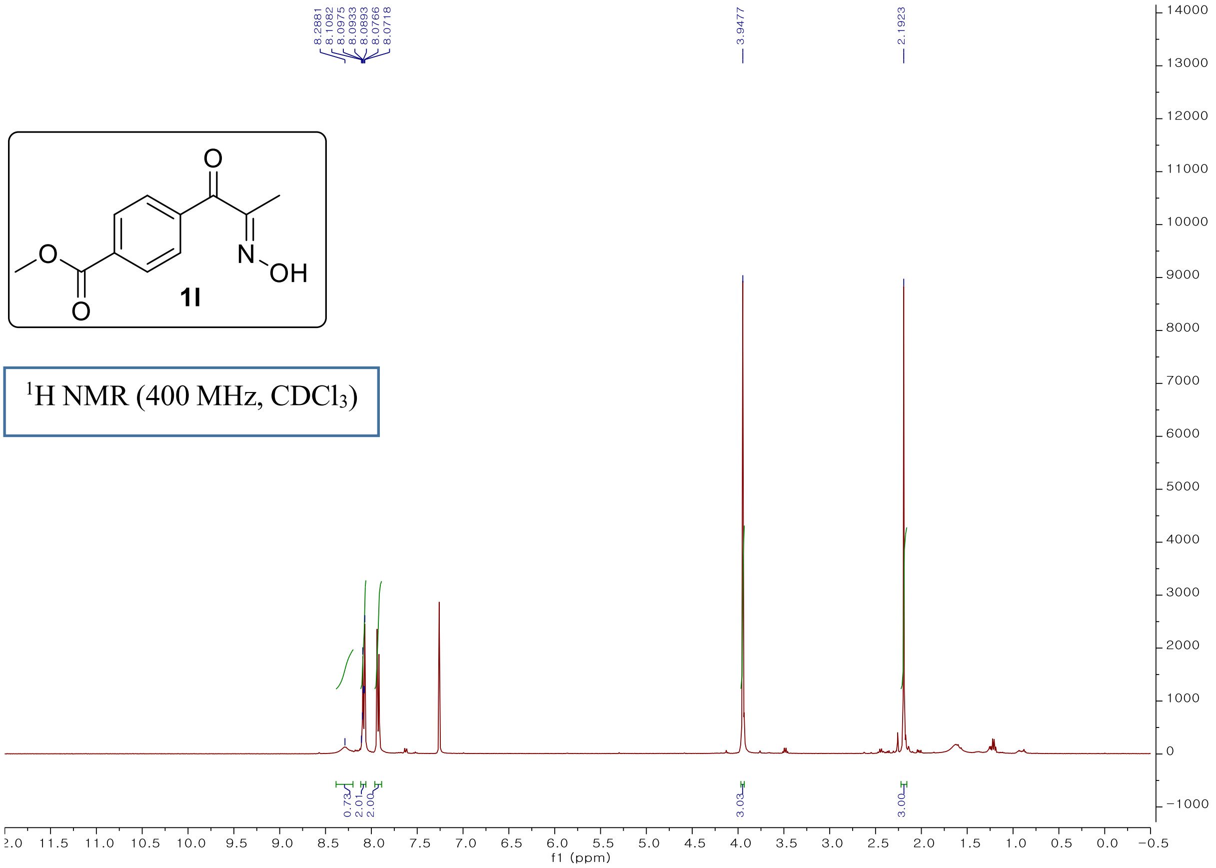


**1k**

$^{1}$H NMR (500 MHz, $CDCl_3$)

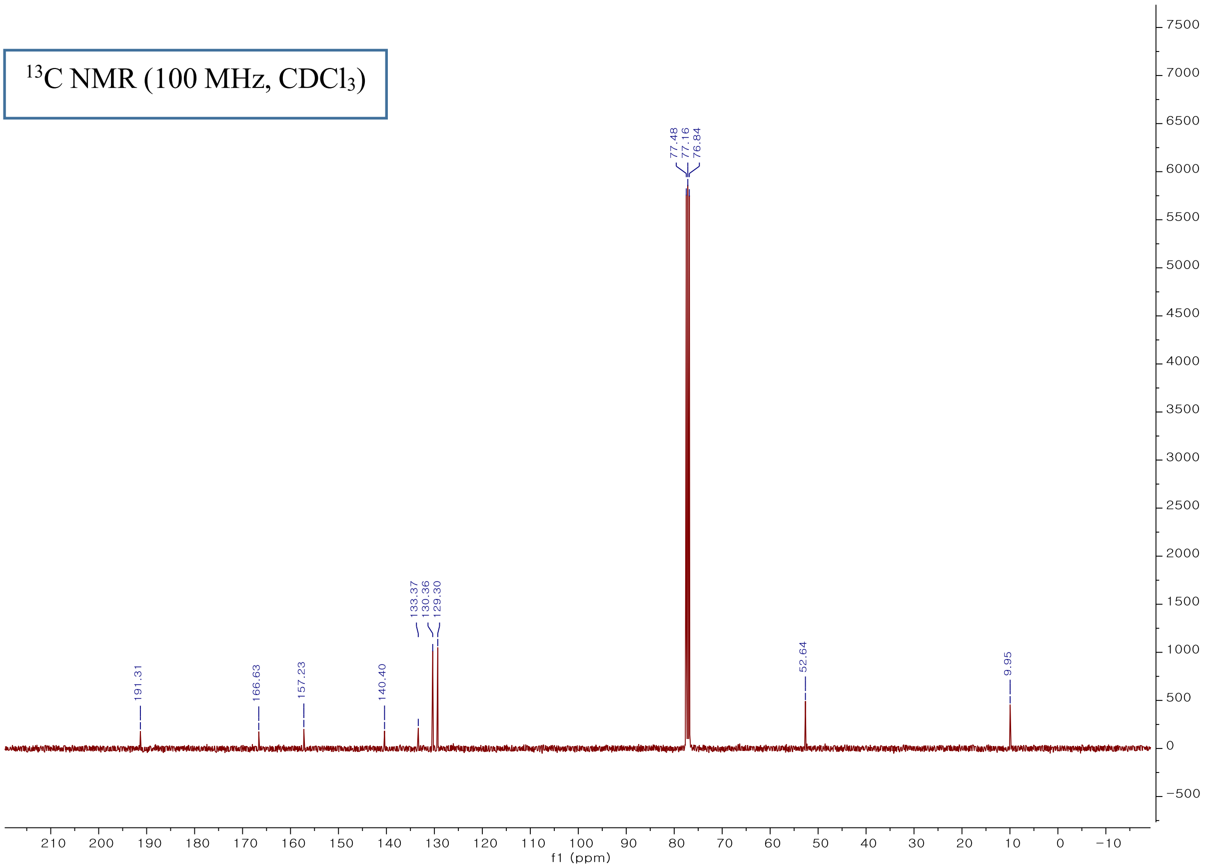


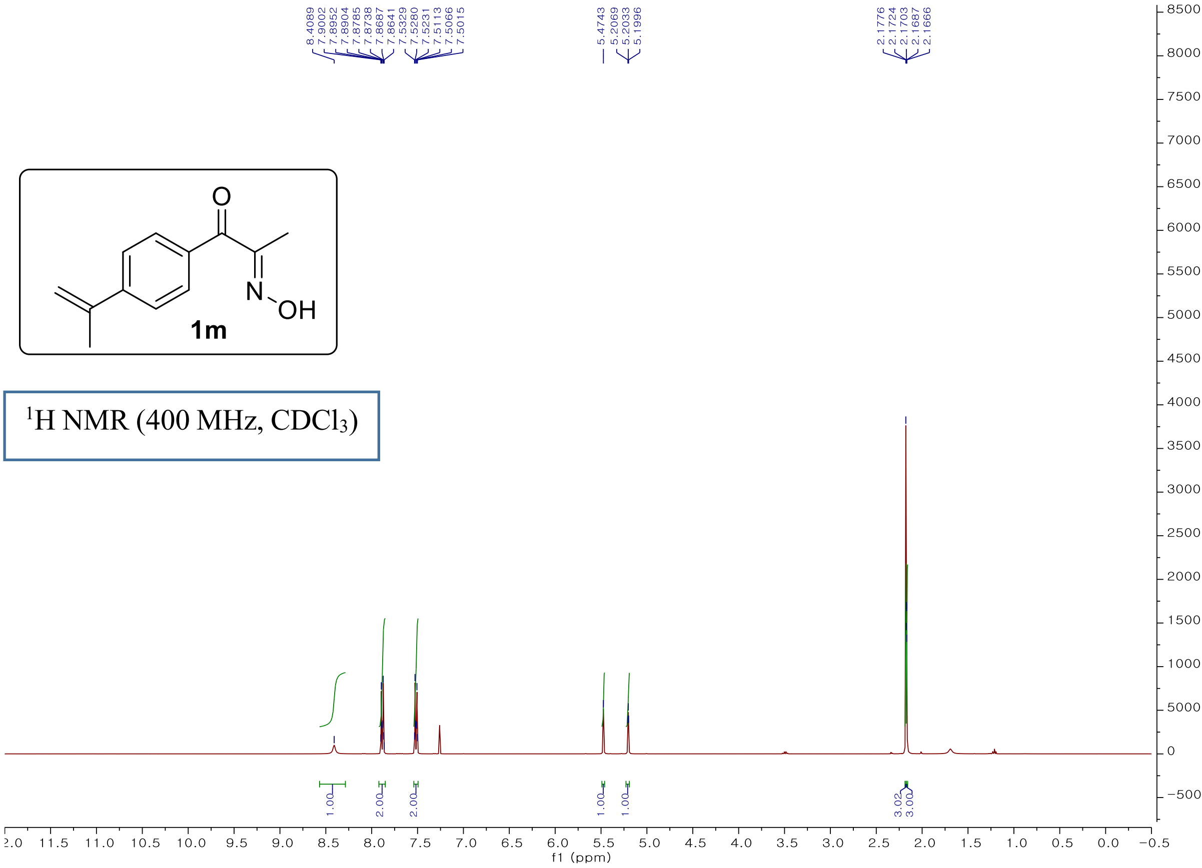
$^{13}$C NMR (100 MHz, $CDCl_3$)



$^{1}$H NMR (400 MHz, CDCl$_3$)

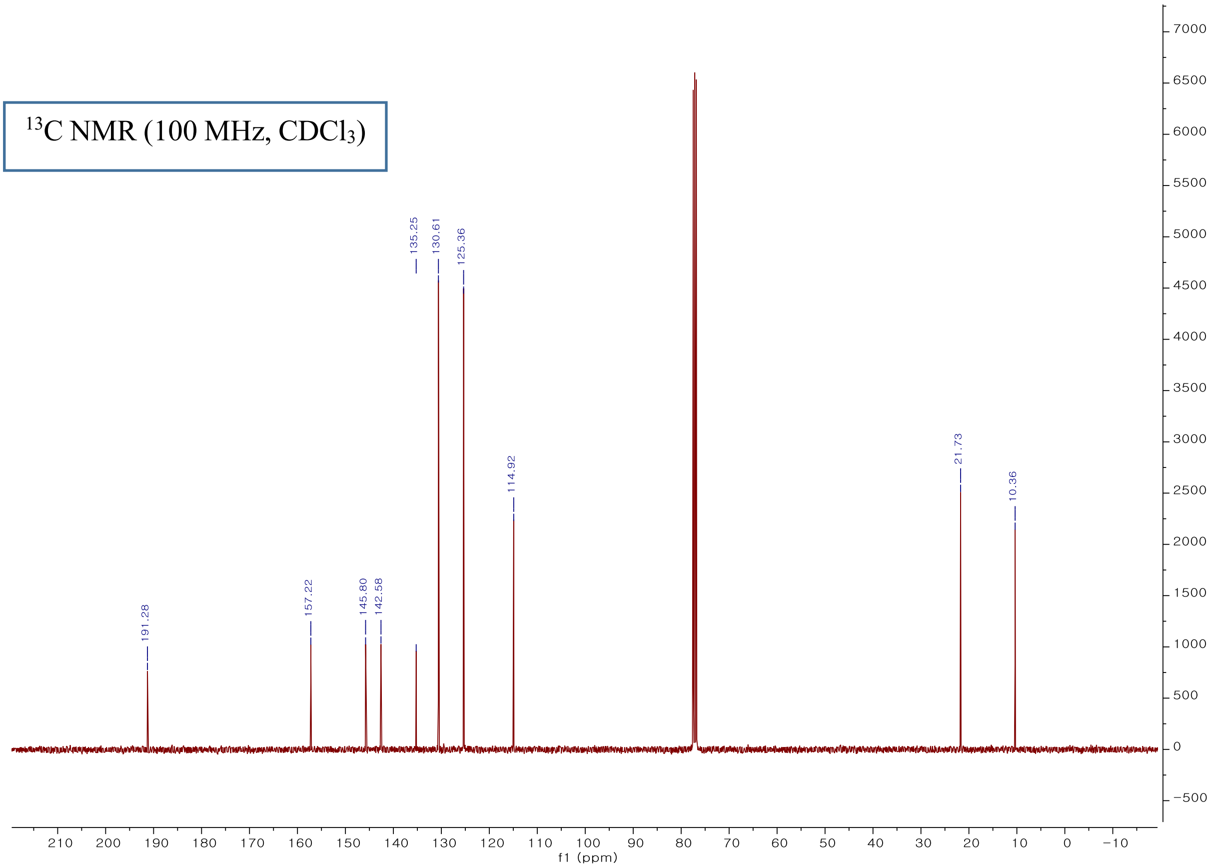
$^{13}$C NMR (100 MHz, CDCl$_3$)



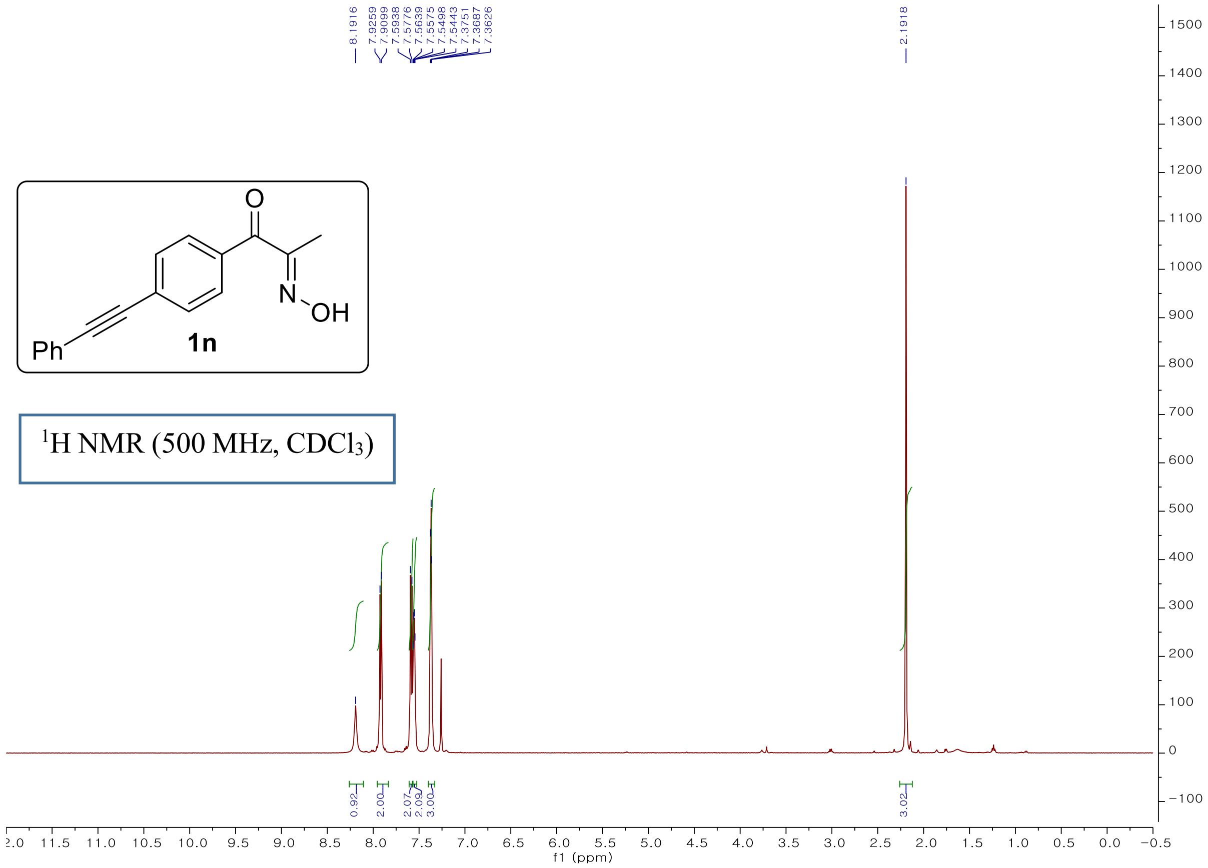


**1m**

$^{1}$H NMR (400 MHz, CDCl$_3$)

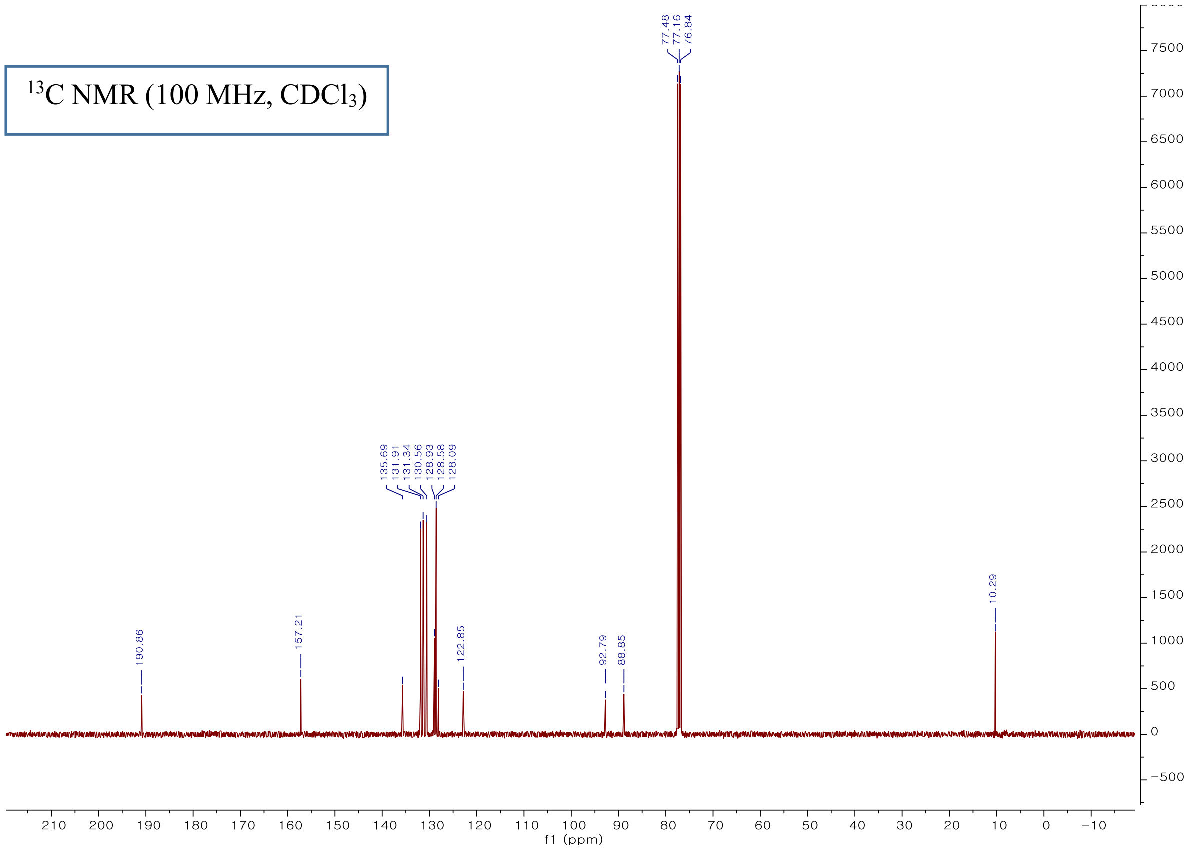


$^{13}$C NMR (100 MHz, CDCl$_3$)

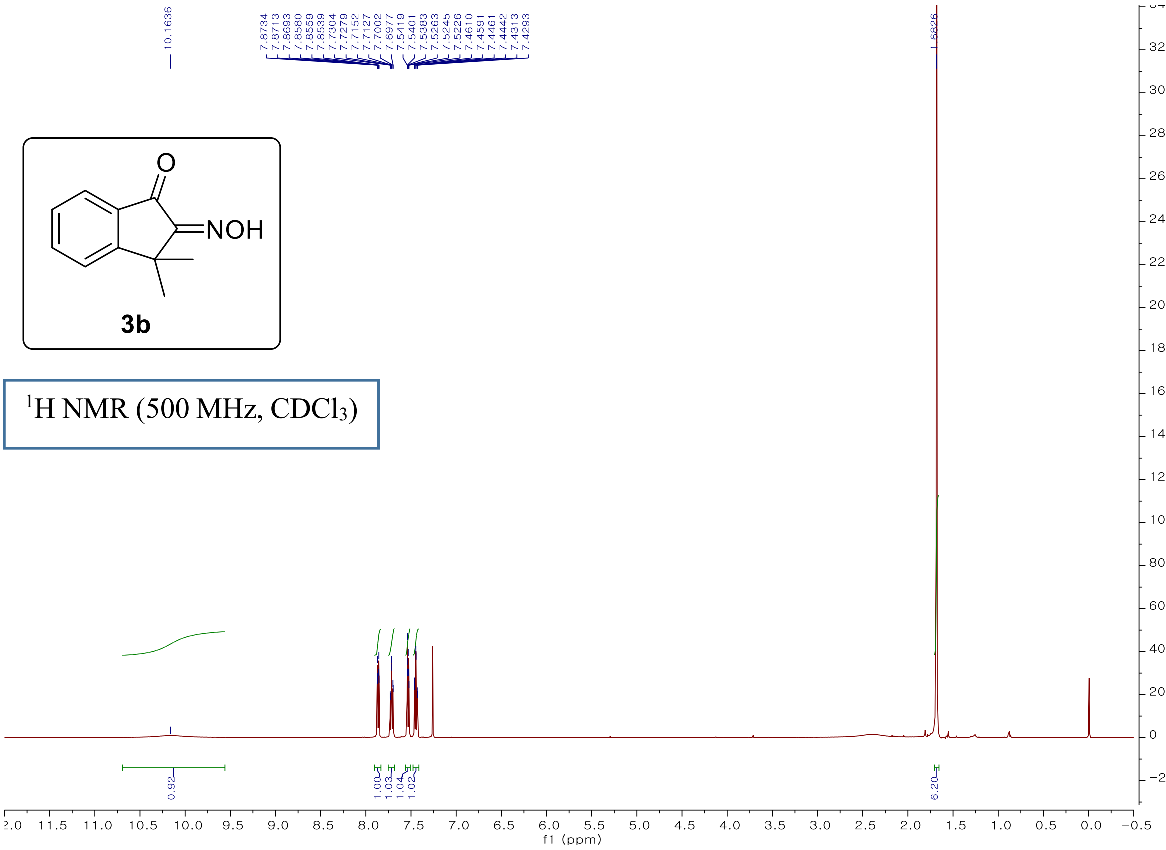


**1n**

$^1$H NMR (500 MHz, $CDCl_3$)

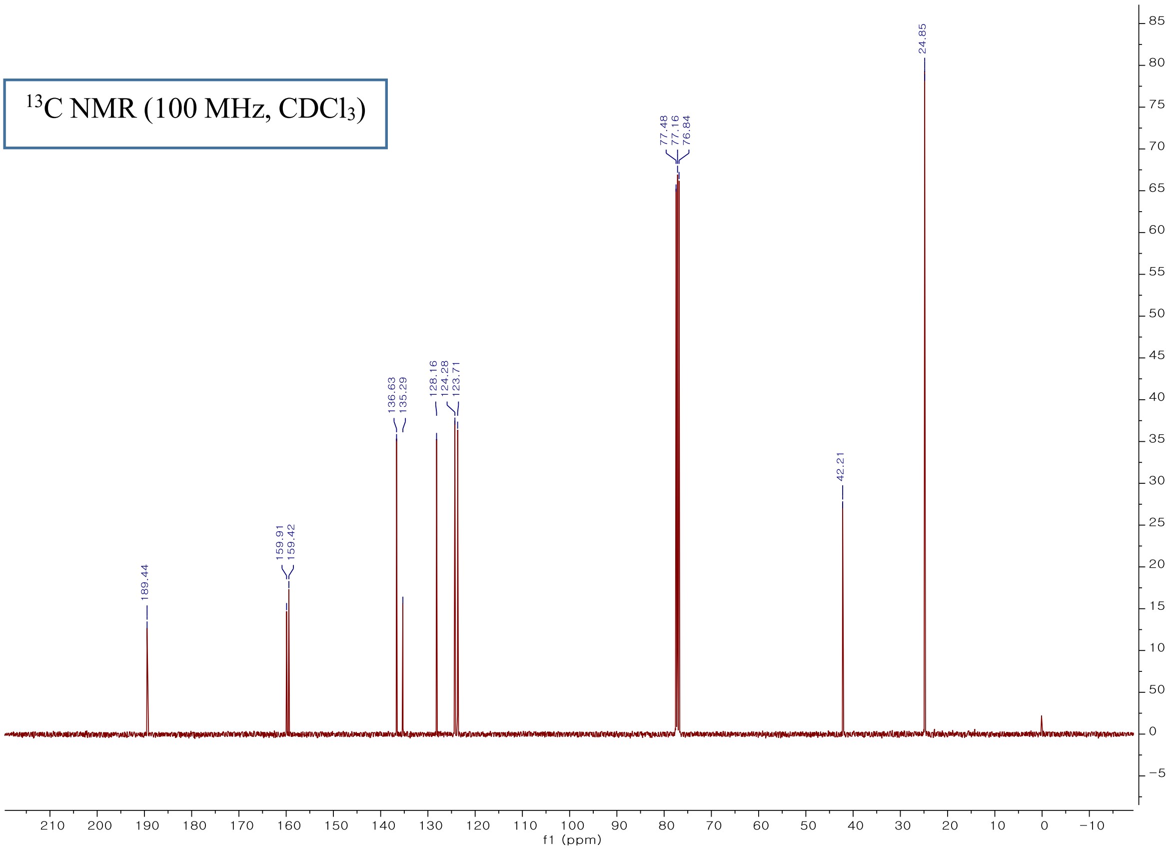


$^{13}$C NMR (100 MHz, $CDCl_3$)

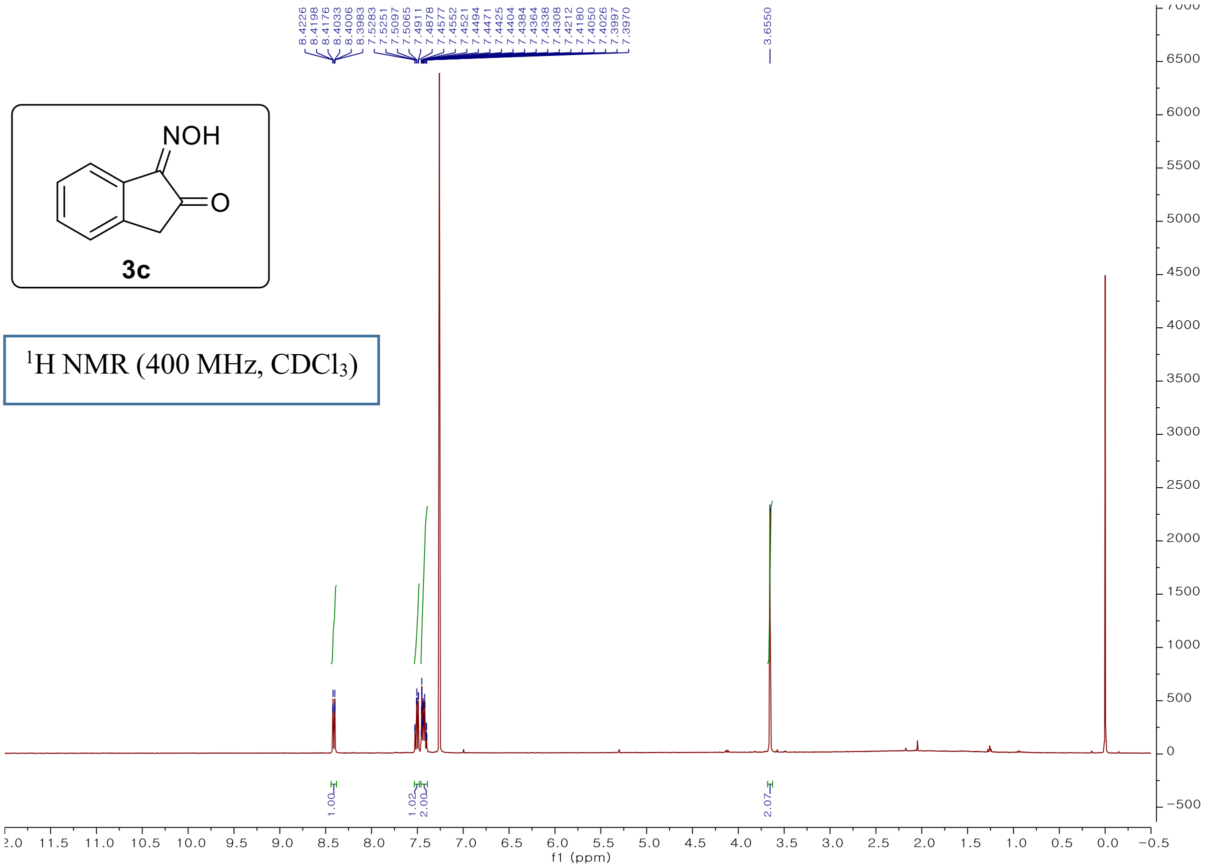


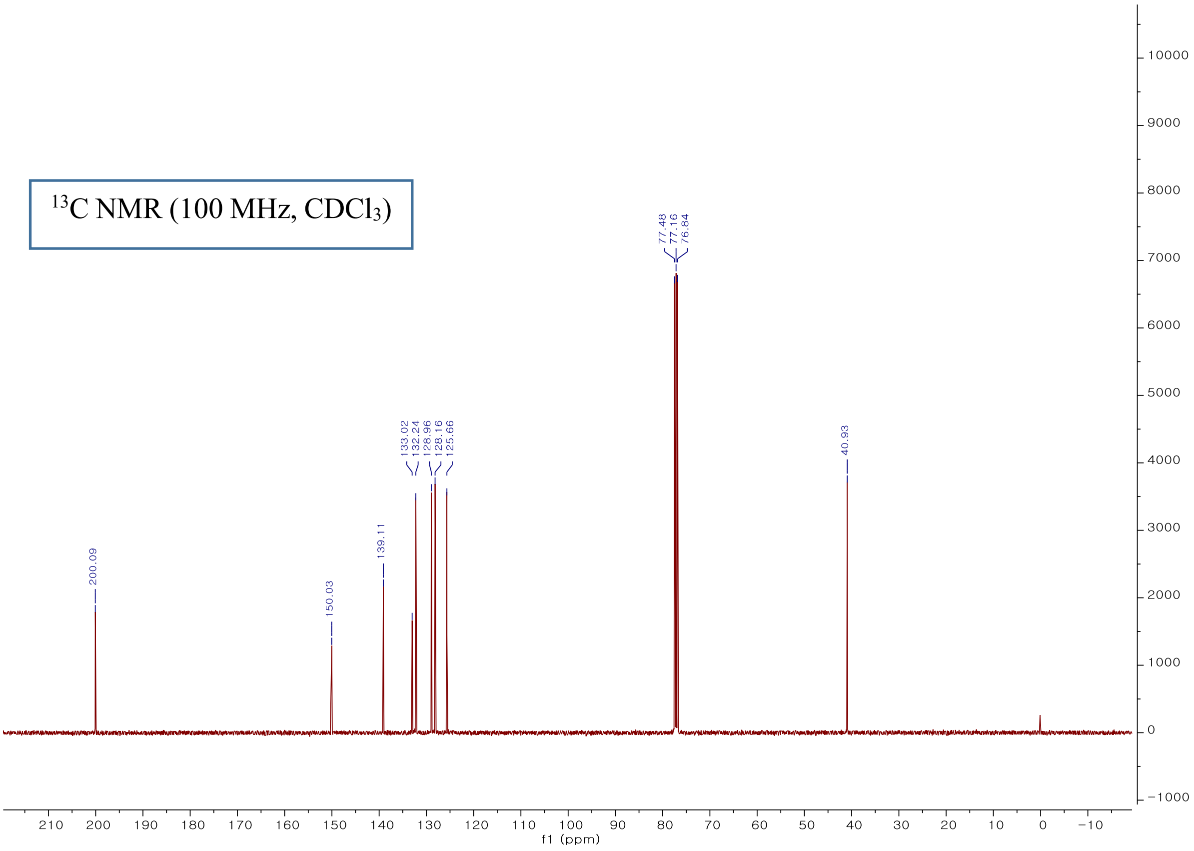
**3b**

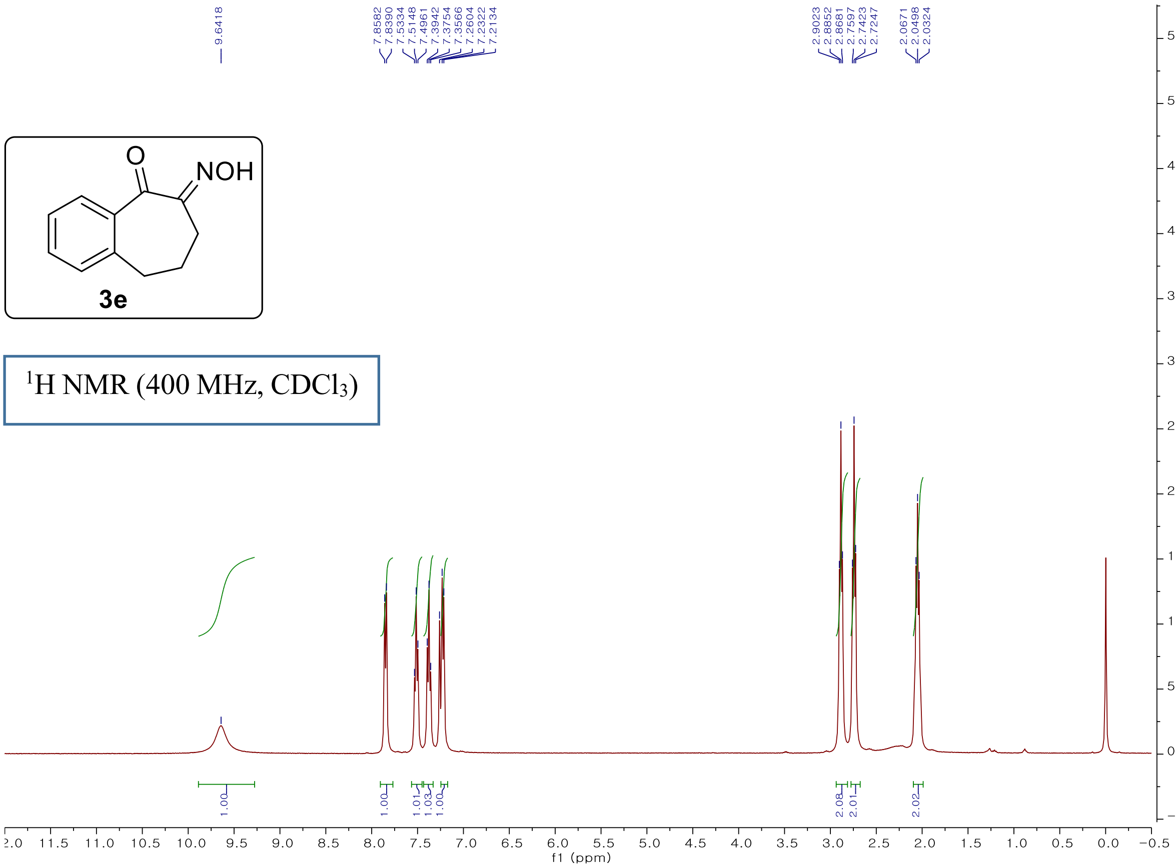
$^1$H NMR (500 MHz, CDCl$_3$)

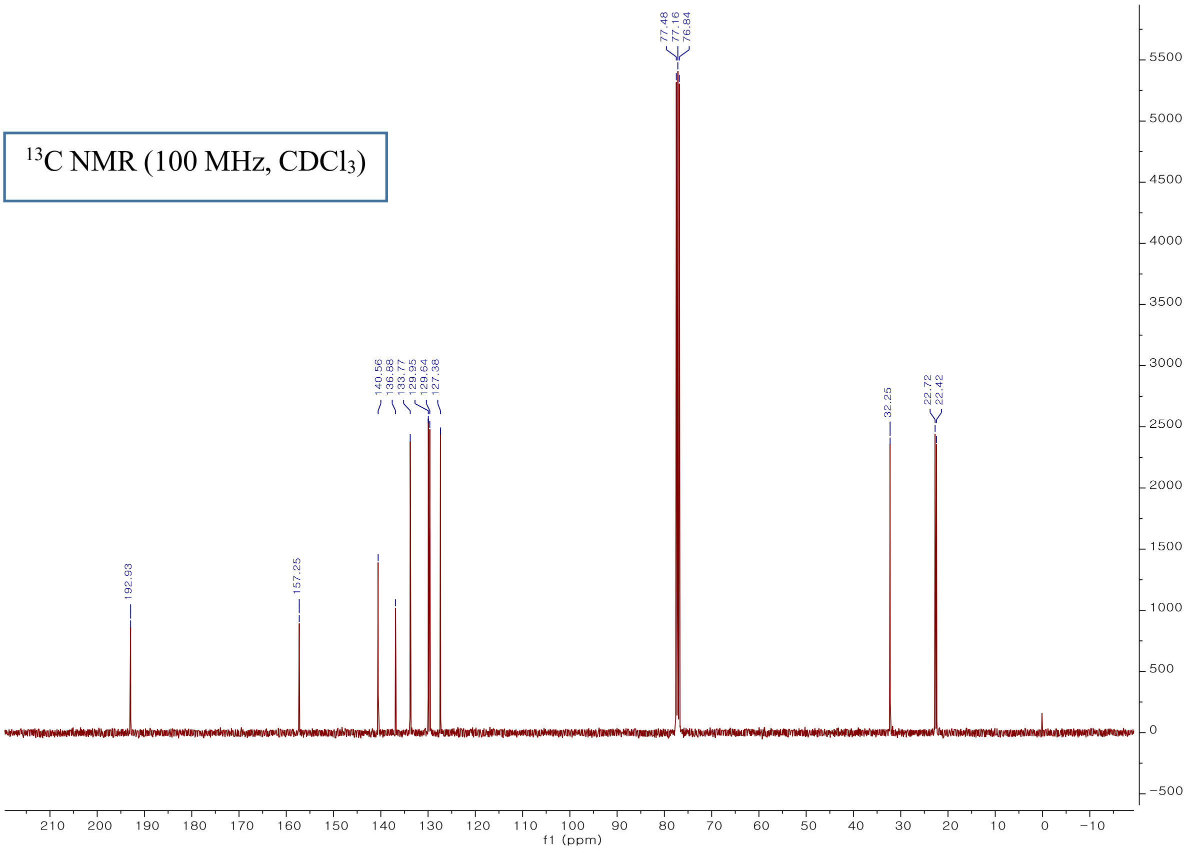


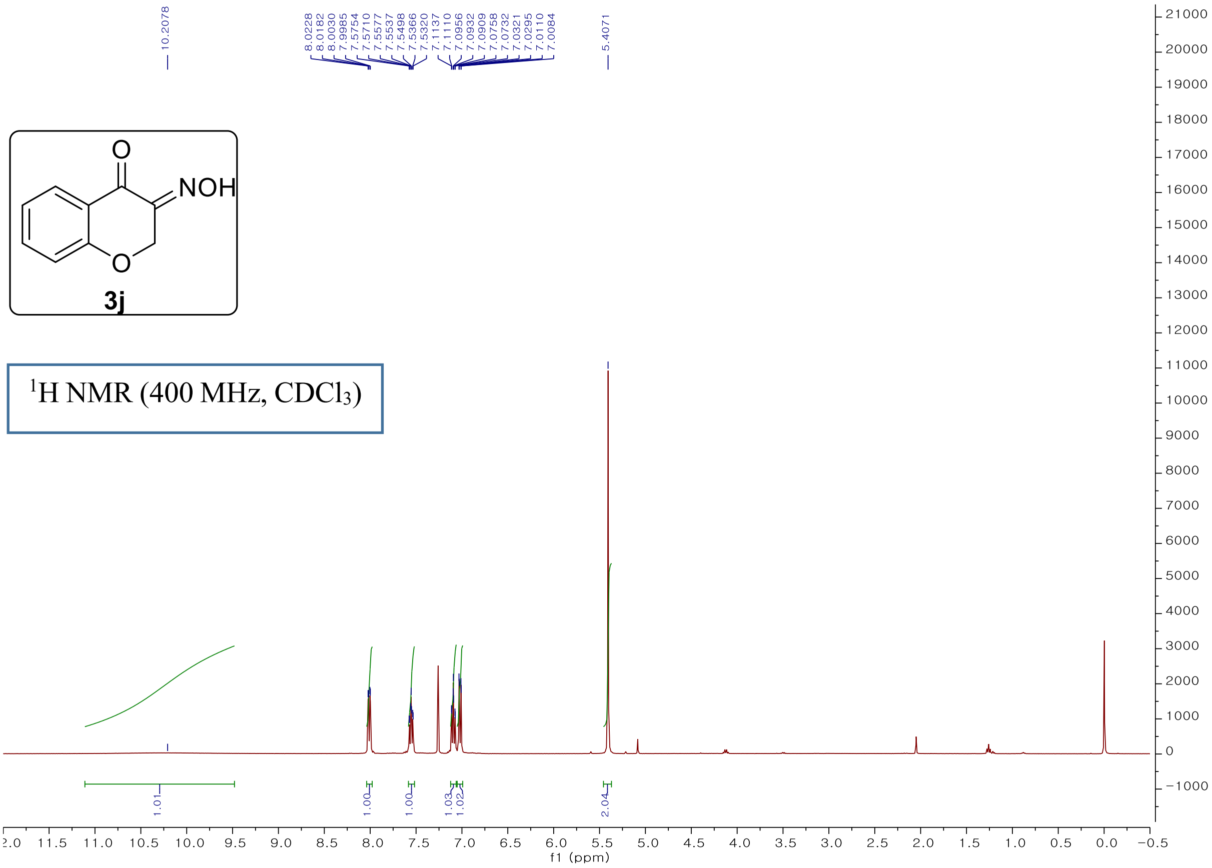
$^{13}$C NMR (100 MHz, CDCl$_3$)


NOH
O
3c
¹H NMR (400 MHz, CDCl₃)
8.4226
8.4198
8.4176
8.4033
8.4006
8.3983
7.5283
7.5251
7.5097
7.5065
7.4911
7.4878
7.4577
7.4552
7.4521
7.4494
7.4471
7.4425
7.4404
7.4384
7.4364
7.4338
7.4308
7.4212
7.4180
7.4050
7.4026
7.3997
7.3970
3.6550
1.00
1.02
2.00
2.07
f1 (ppm)


¹³C NMR (100 MHz, CDCl₃)
200.09
150.03
139.11
133.02
132.24
128.96
128.16
125.66
77.48
77.16
76.84
40.93
f1 (ppm)

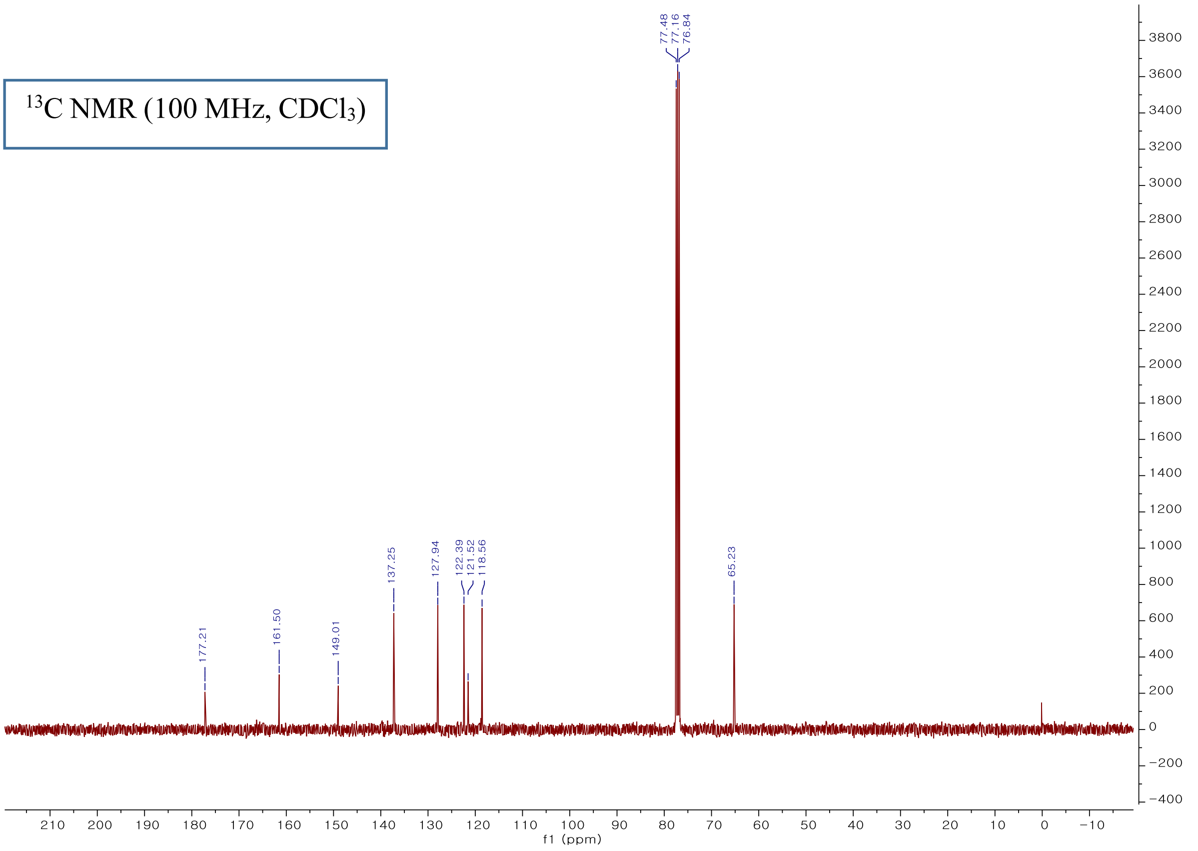

9.6418
7.8582
7.8390
7.5334
7.5148
7.4961
7.3942
7.3754
7.3566
7.2604
7.2322
7.2134
2.9023
2.8852
2.8681
2.7597
2.7423
2.7247
2.0671
2.0498
2.0324
O
NOH
3e
$^1$H NMR (400 MHz, CDCl$_3$)
1.00
1.00
1.01
1.03
1.00
2.08
2.01
2.02
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


77.48
77.16
76.84
$^{13}$C NMR (100 MHz, CDCl$_3$)
140.56
136.88
133.77
129.95
129.64
127.38
32.25
22.72
22.42
192.93
157.25
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

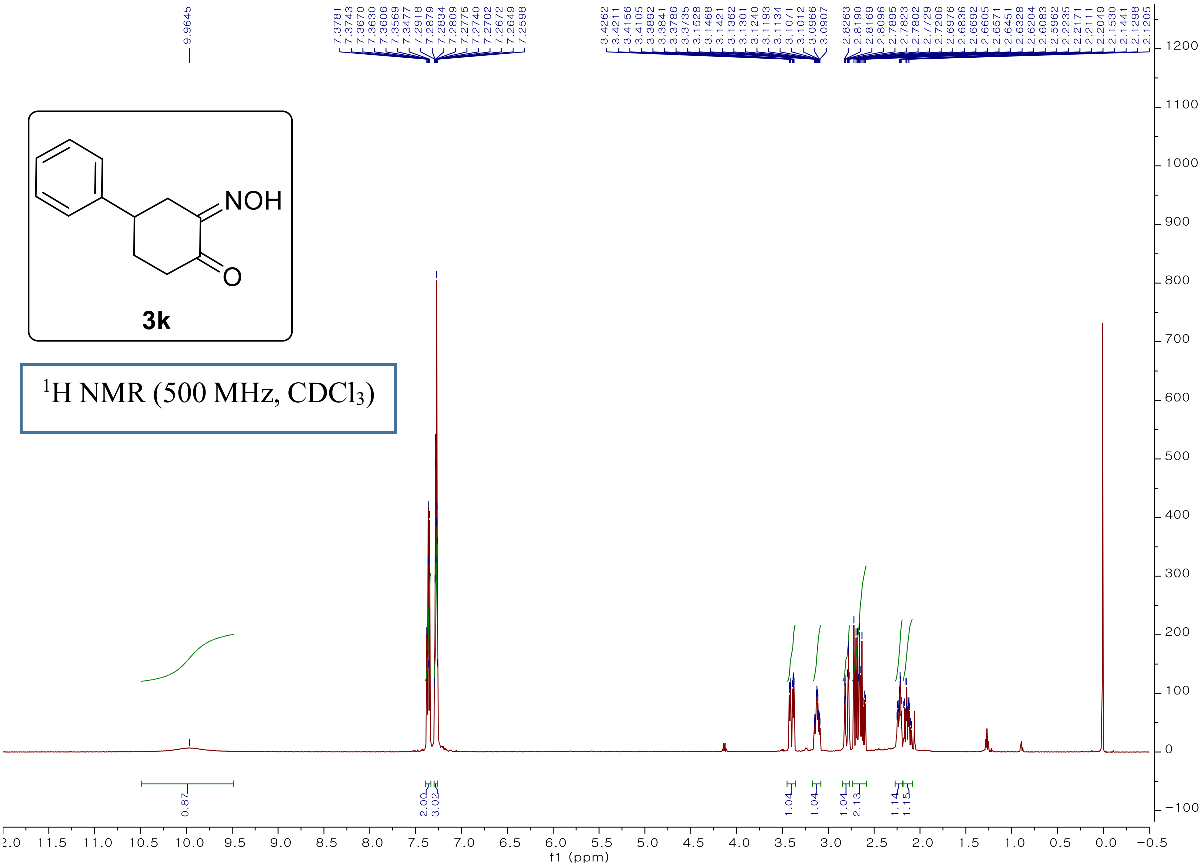


**3j**

$^1$H NMR (400 MHz, CDCl$_3$)

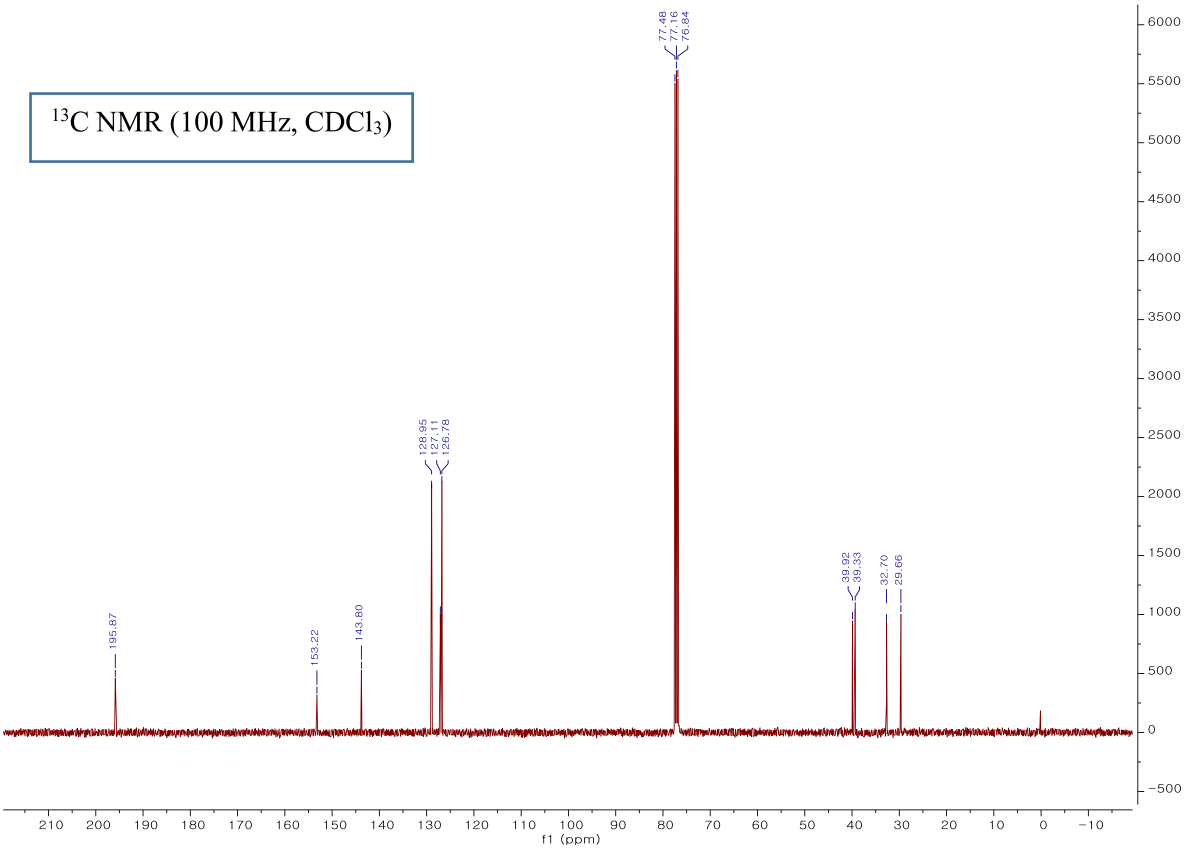


$^{13}$C NMR (100 MHz, CDCl$_3$)

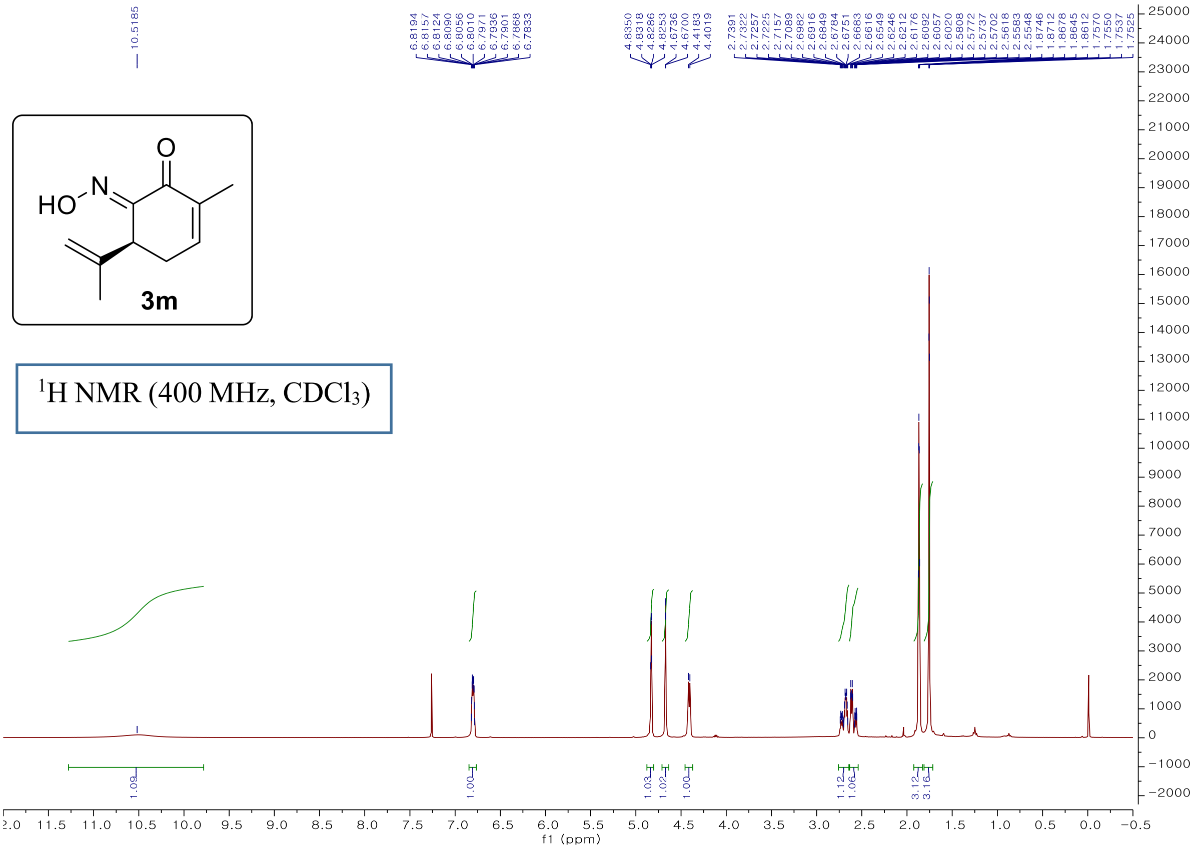


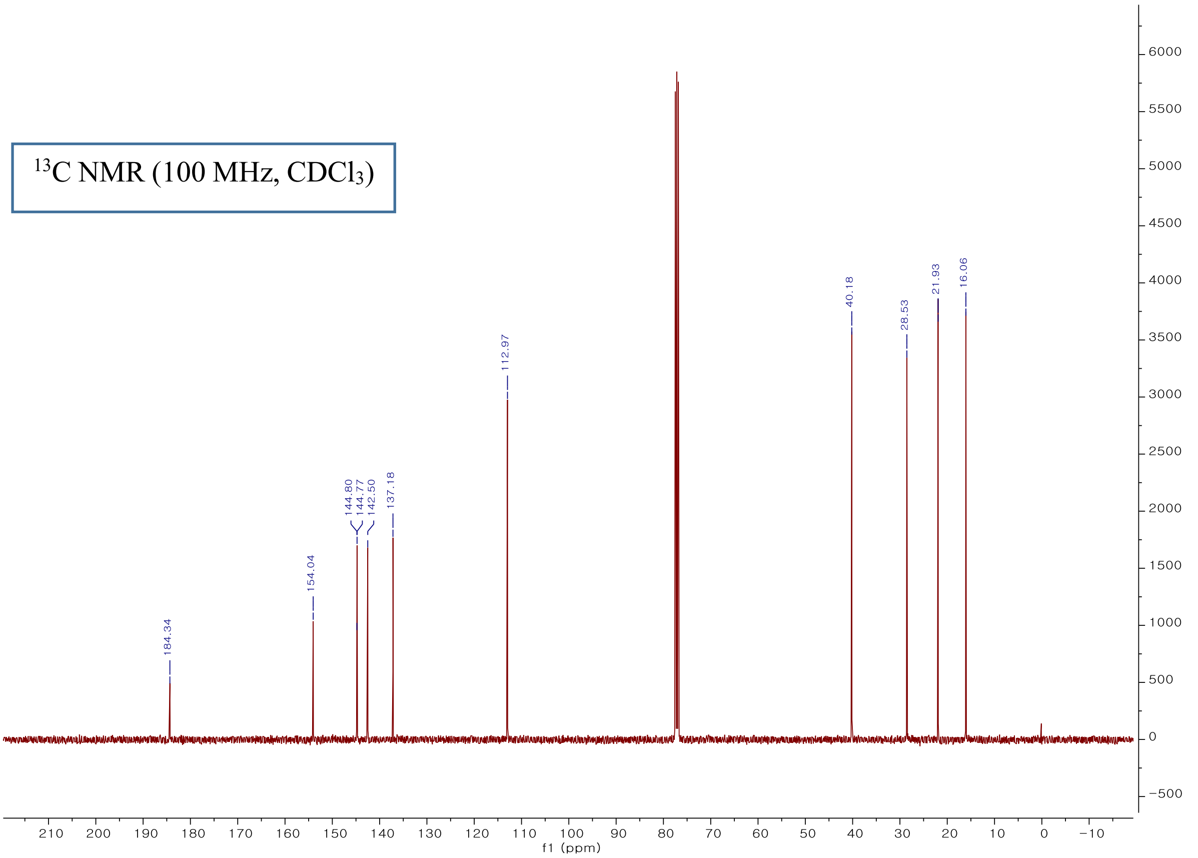
3k

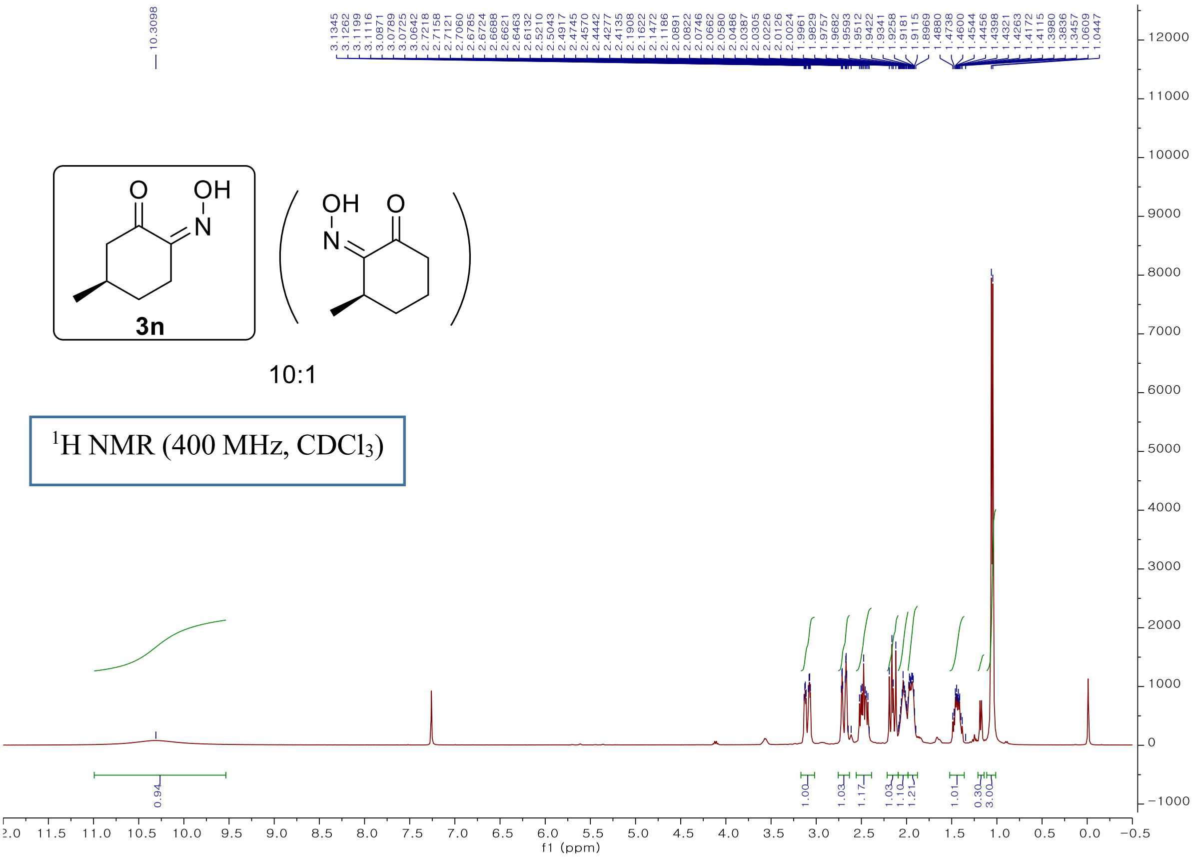
$^{1}$H NMR (500 MHz, CDCl$_3$)



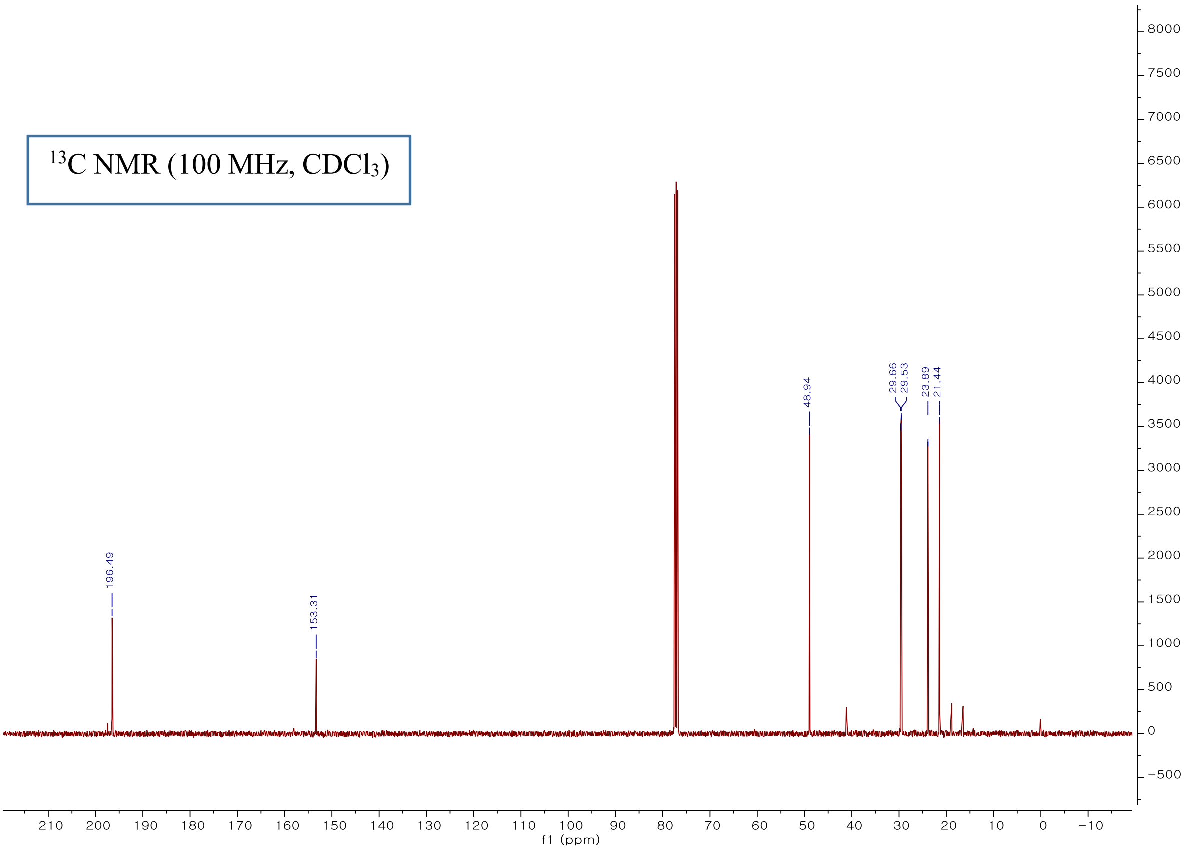
$^{13}$C NMR (100 MHz, CDCl$_3$)


HO
N
O
3m
$^1$H NMR (400 MHz, CDCl$_3$)
10.5185
6.8194
6.8157
6.8124
6.8090
6.8056
6.8010
6.7971
6.7936
6.7901
6.7868
6.7833
4.8350
4.8318
4.8286
4.8253
4.6776
4.6700
4.4183
4.4019
2.7391
2.7322
2.7257
2.7225
2.7157
2.7089
2.6982
2.6916
2.6849
2.6784
2.6751
2.6683
2.6616
2.6549
2.6246
2.6212
2.6176
2.6092
2.6057
2.6020
2.5808
2.5772
2.5737
2.5702
2.5618
2.5583
2.5548
1.8746
1.8712
1.8678
1.8645
1.8612
1.7570
1.7550
1.7537
1.7525
1.09
1.00
1.03
1.02
1.00
1.12
1.06
3.12
3.16
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

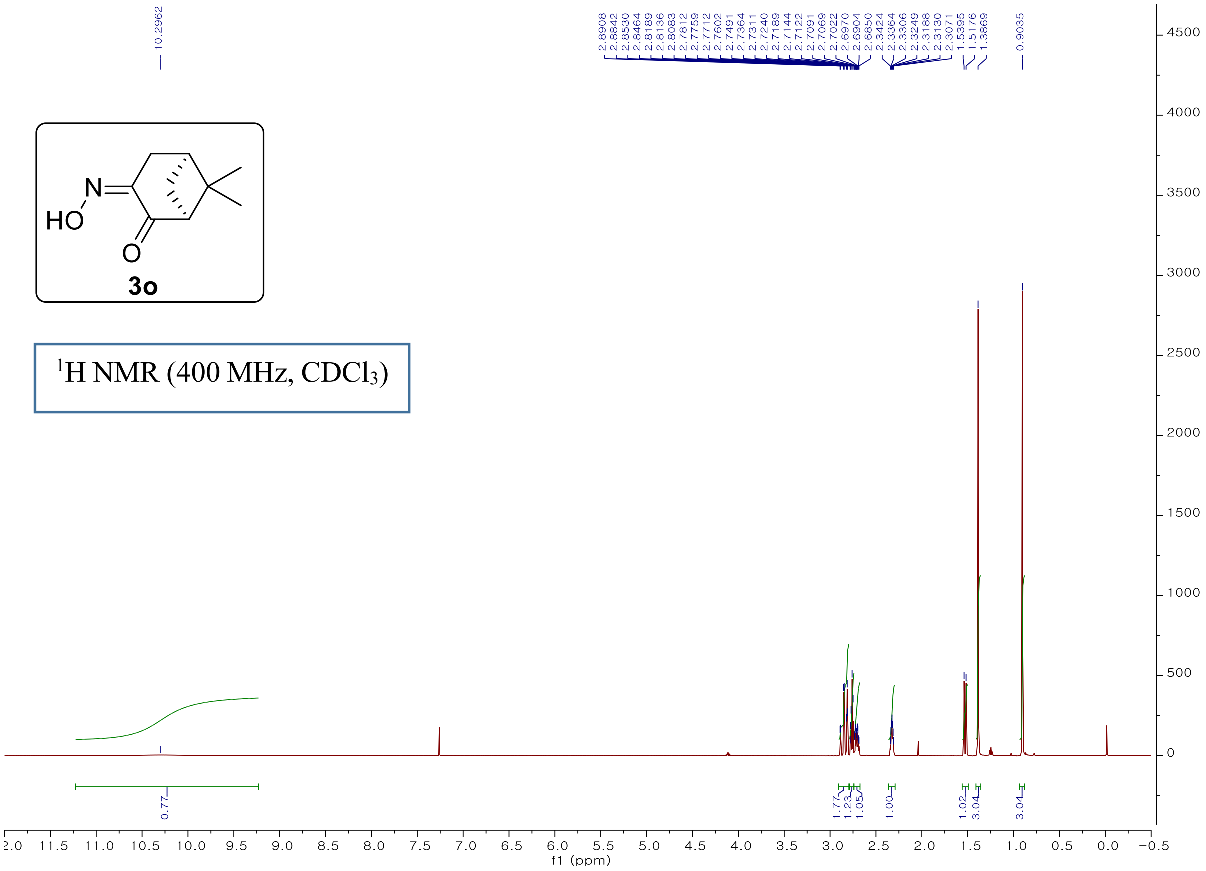

$^{13}$C NMR (100 MHz, CDCl$_3$)
184.34
154.04
144.80
144.77
142.50
137.18
112.97
40.18
28.53
21.93
16.06
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



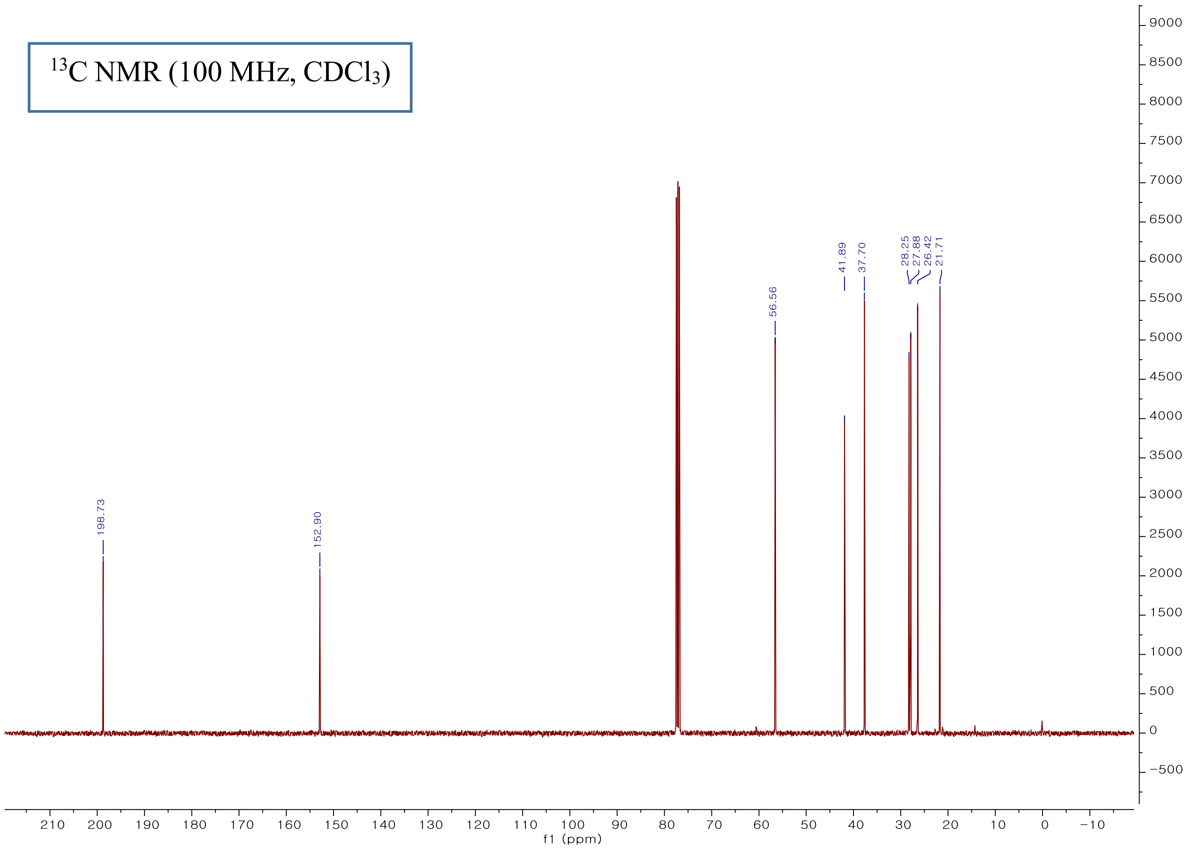
$^1$H NMR (400 MHz, CDCl$_3$)



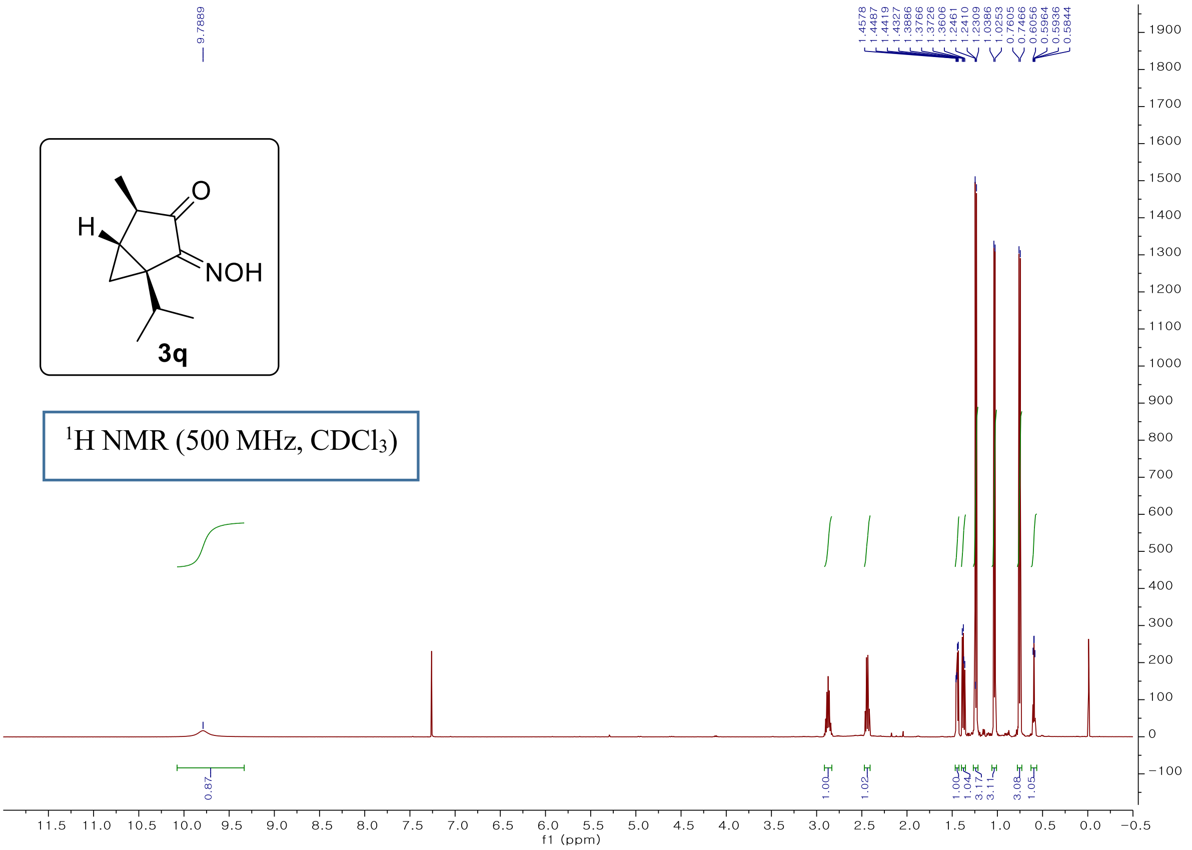
$^{13}$C NMR (100 MHz, CDCl$_3$)



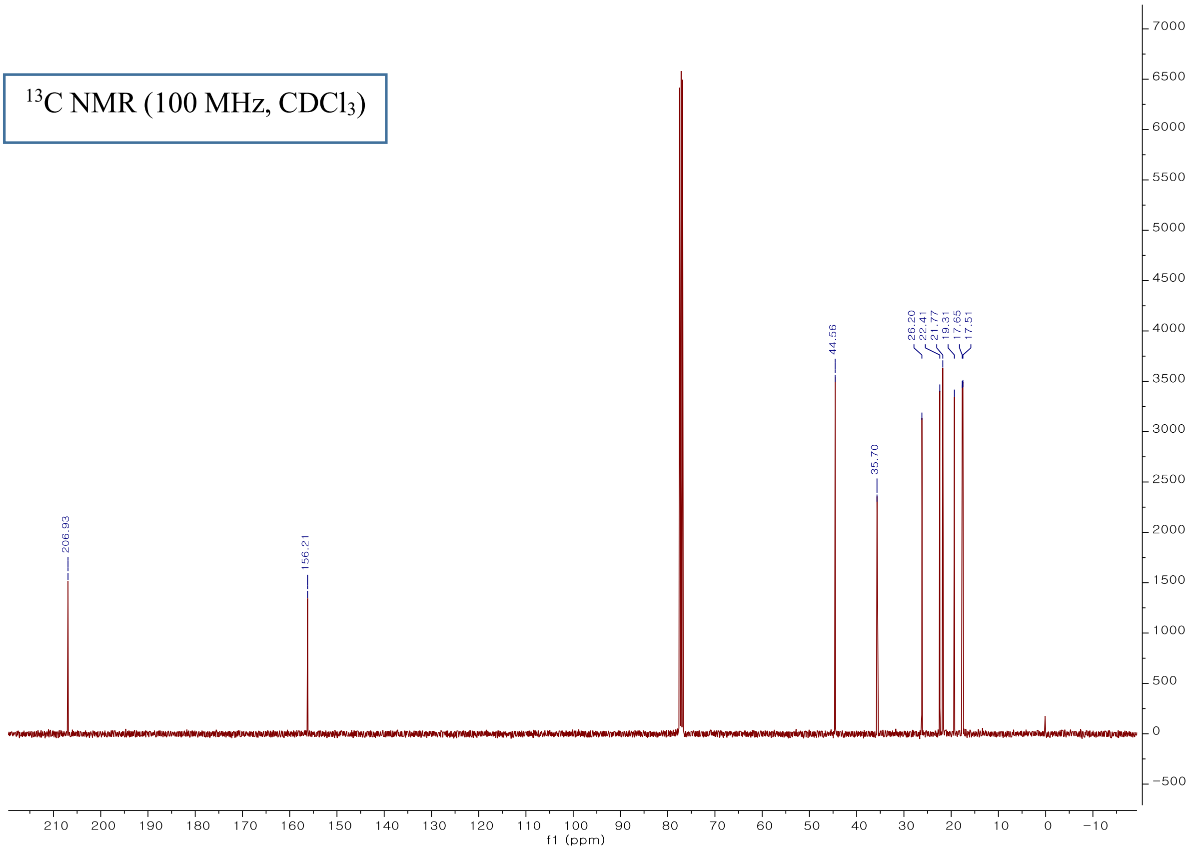
$^1$H NMR (400 MHz, CDCl$_3$)

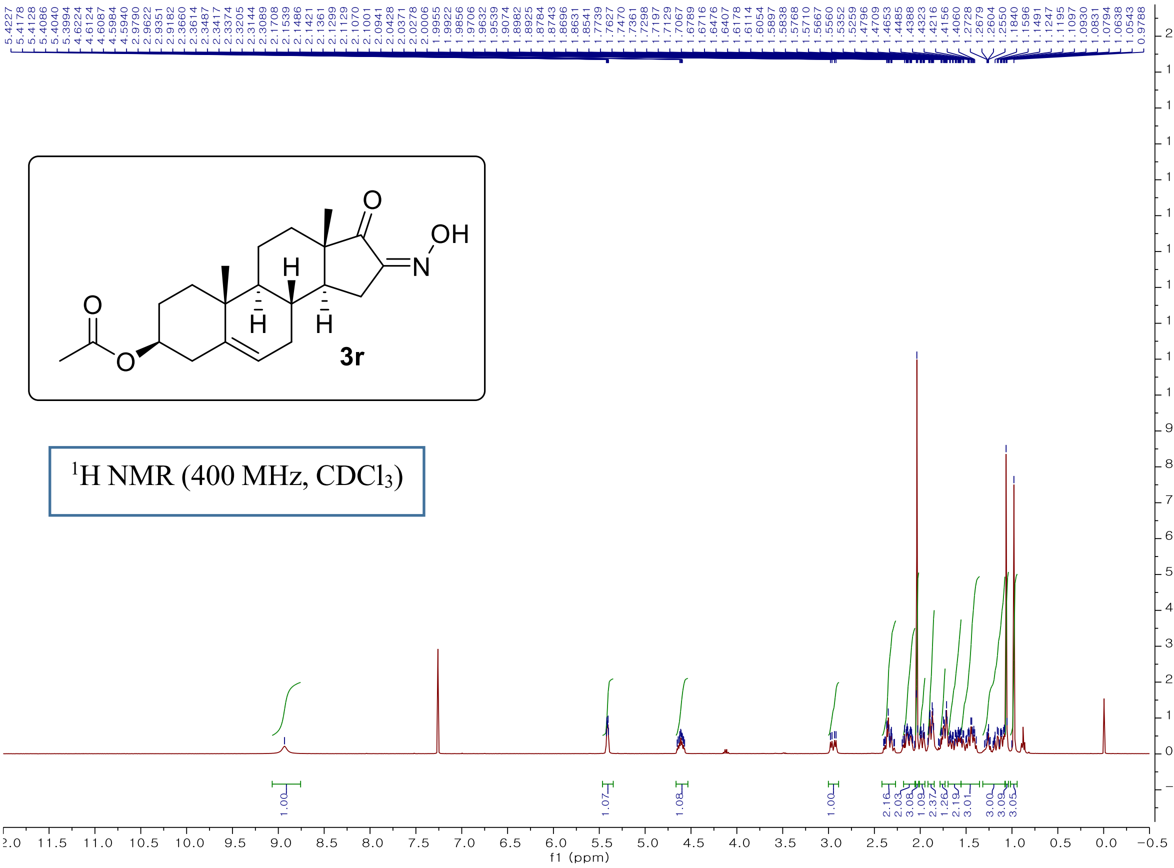


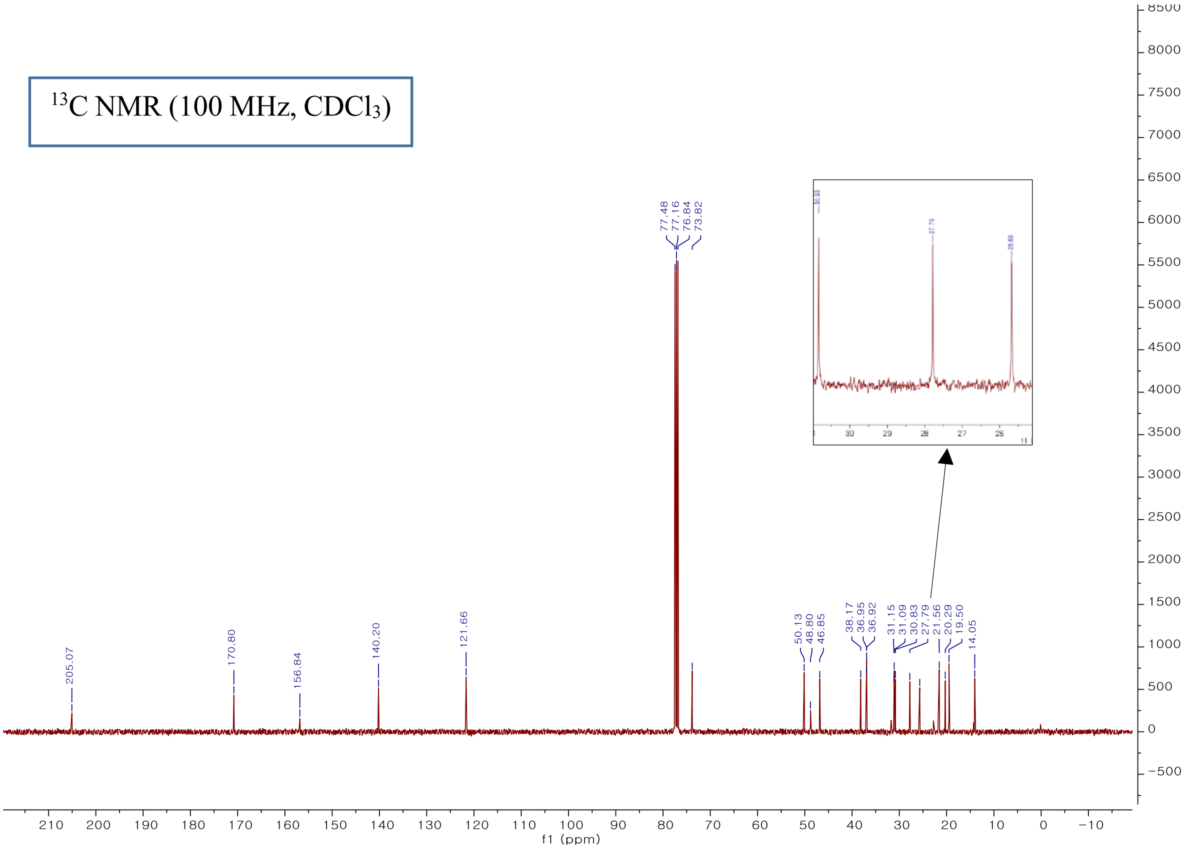
$^{13}$C NMR (100 MHz, CDCl$_3$)

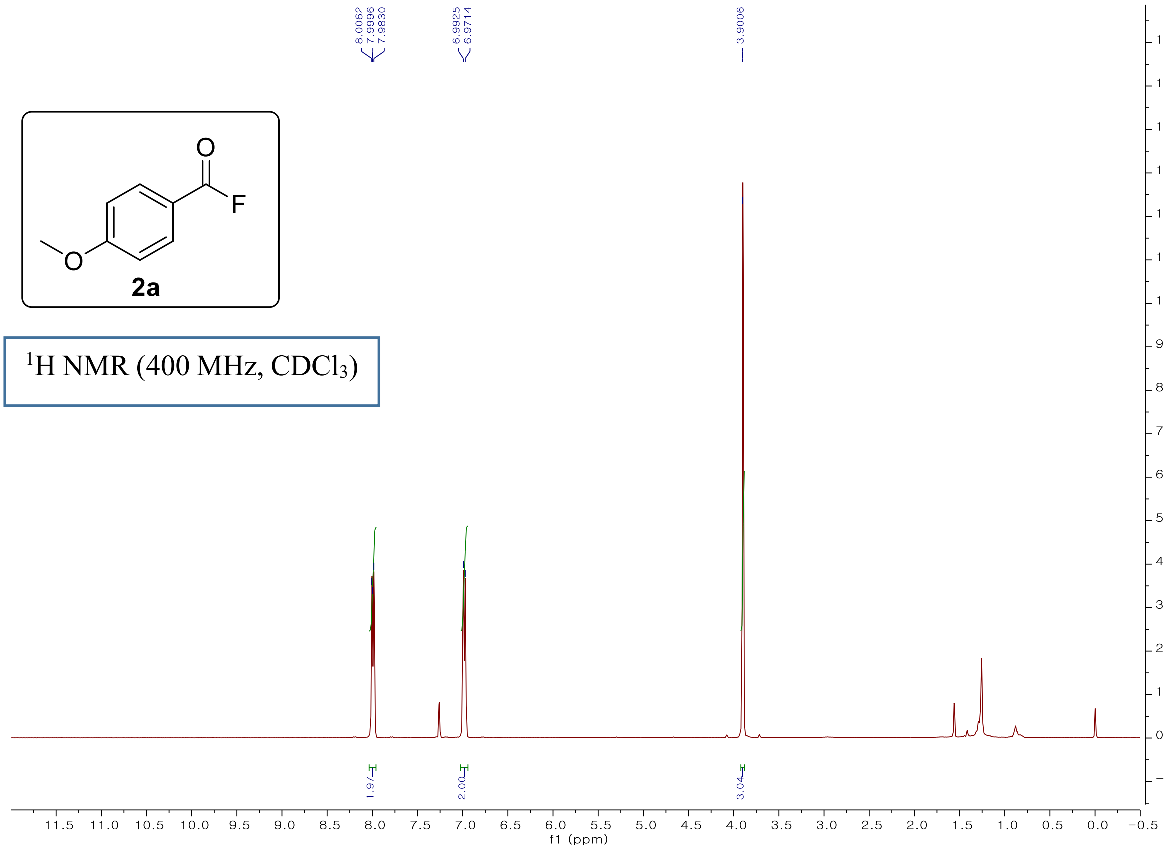

**3q**

$^{1}$H NMR (500 MHz, CDCl$_3$)

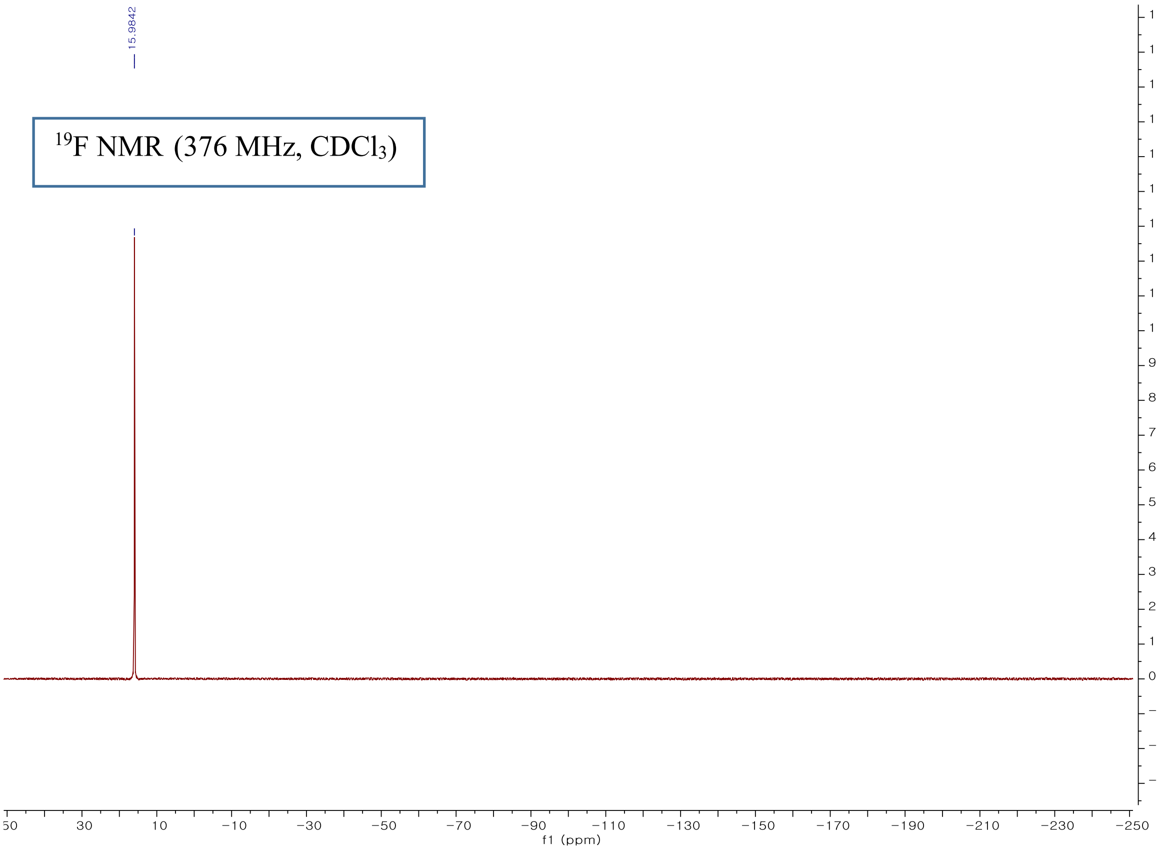

$^{13}$C NMR (100 MHz, CDCl$_3$)

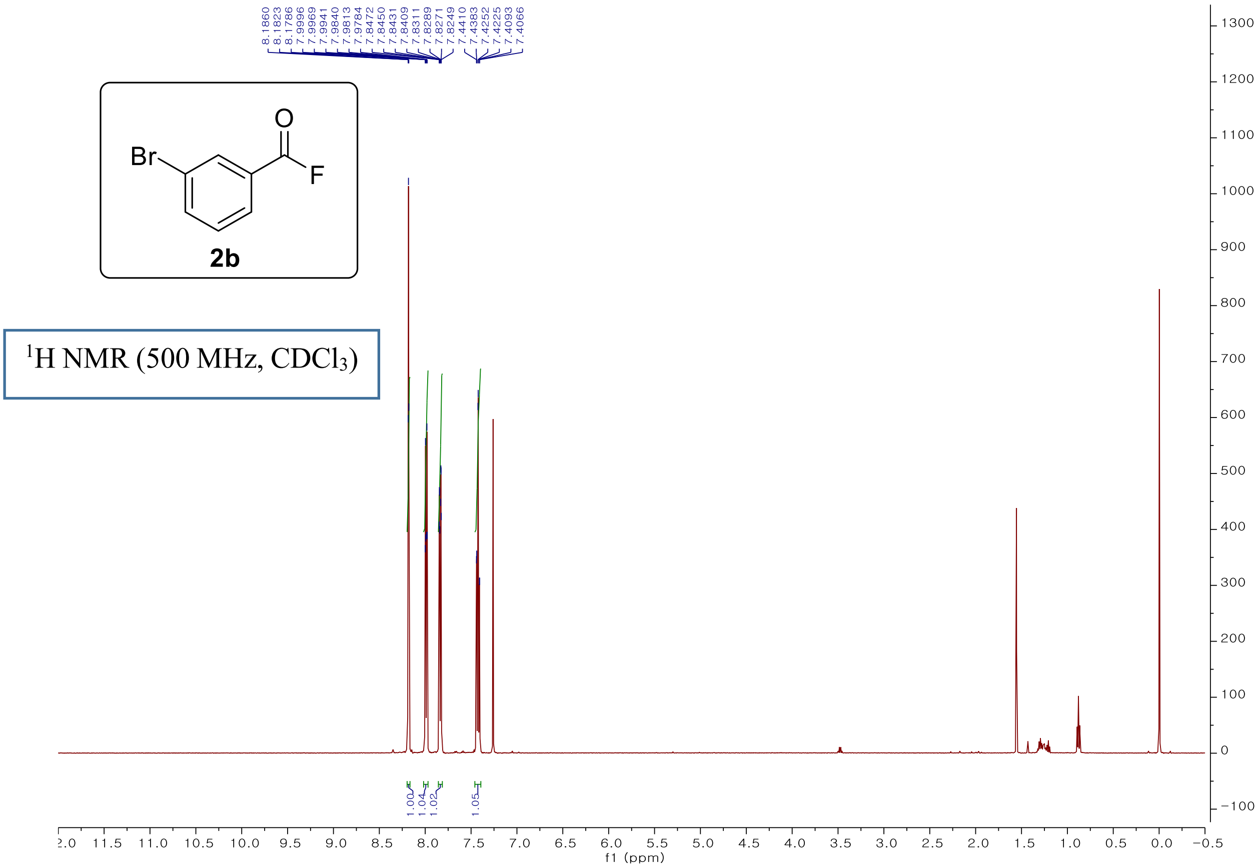

5.4227
5.4178
5.4086
5.4040
5.3994
4.6224
4.6124
4.6087
4.5984
4.5940
2.9790
2.9622
2.9351
2.9182
2.3660
2.3614
2.3487
2.3374
2.3205
2.3144
2.3089
2.1708
2.1539
2.1486
2.1421
2.1361
2.1299
2.1129
2.1070
2.1001
2.0941
2.0428
2.0371
2.0278
2.0006
1.9955
1.9922
1.9856
1.9706
1.9632
1.9539
1.9074
1.8982
1.8925
1.8784
1.8743
1.8696
1.8631
1.8541
1.7739
1.7627
1.7470
1.7361
1.7298
1.7197
1.7129
1.7067
1.6789
1.6716
1.6476
1.6407
1.6178
1.6114
1.6054
1.5897
1.5838
1.5768
1.5710
1.5667
1.5560
1.5352
1.5259
1.4796
1.4709
1.4653
1.4485
1.4388
1.4323
1.4216
1.4156
1.4060
1.2728
1.2679
1.2604
1.2550
1.1840
1.1596
1.1491
1.1247
1.1195
1.1097
1.0930
1.0831
1.0794
1.0638
1.0543
0.9788
O
OH
N
H
H
H
O
O
3r
¹H NMR (400 MHz, CDCl₃)
1.00
1.07
1.08
1.00
2.16
2.03
3.08
1.09
2.17
1.26
2.19
3.01
3.00
3.09
3.05
f1 (ppm)


¹³C NMR (100 MHz, CDCl₃)
205.07
170.80
156.84
140.20
121.66
77.48
77.16
76.84
73.82
50.13
48.80
46.85
38.17
36.95
36.92
31.15
31.09
30.83
27.79
21.56
20.29
19.50
14.05
f1 (ppm)

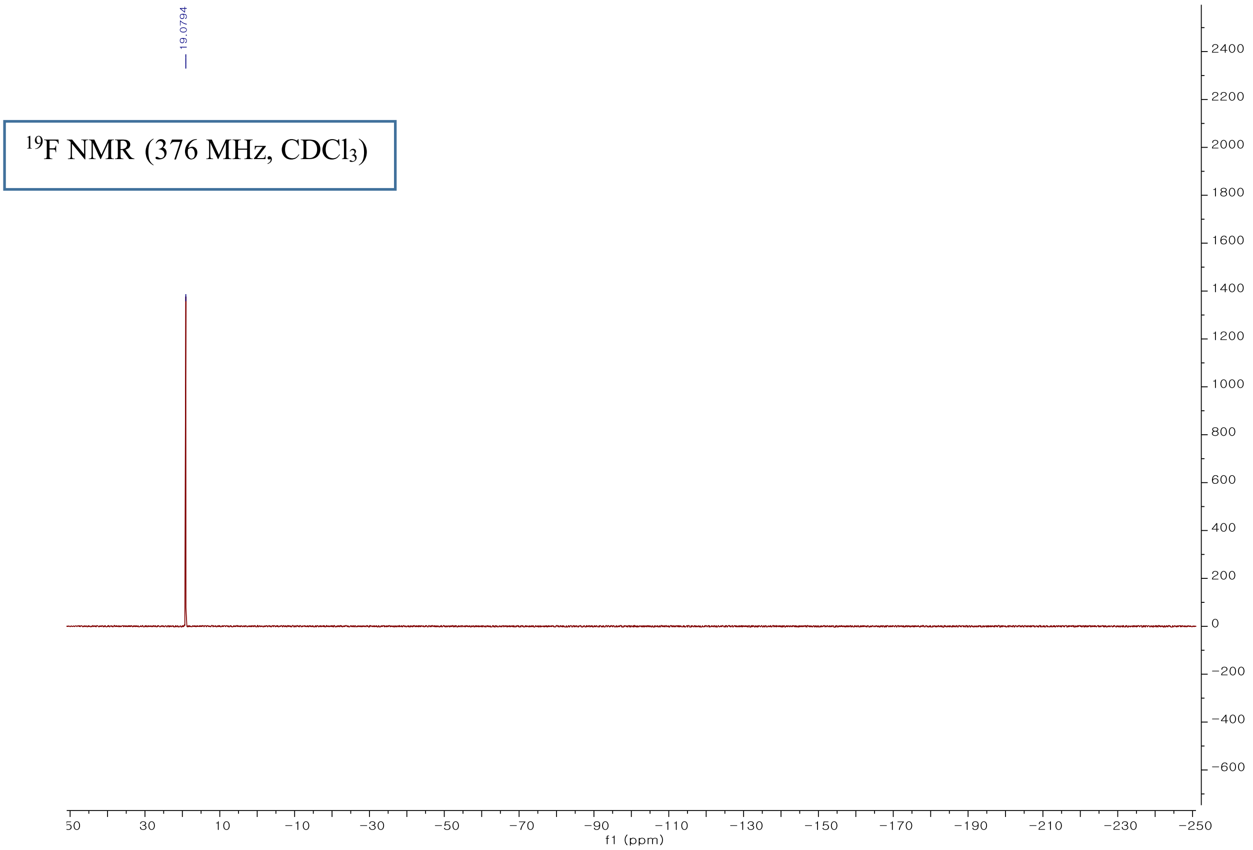

2a

¹H NMR (400 MHz, $CDCl_3$)

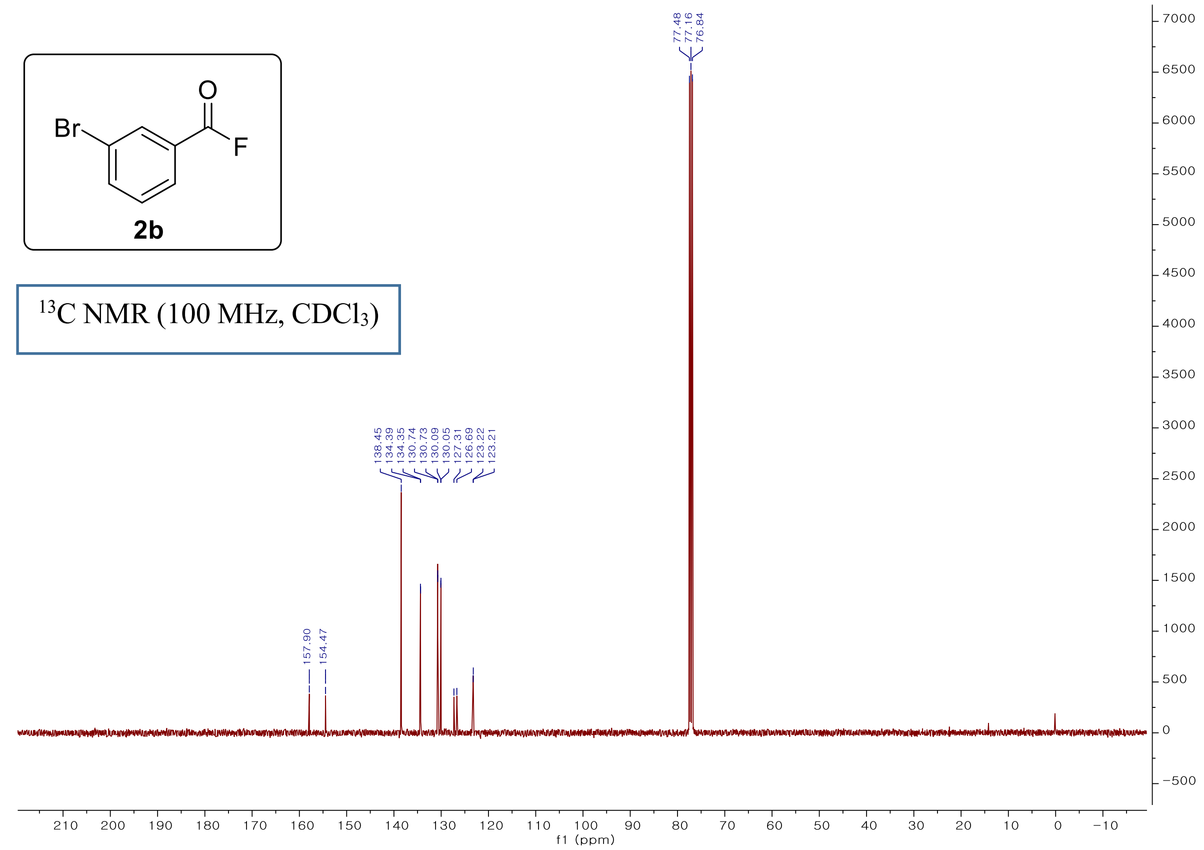

¹⁹F NMR (376 MHz, $CDCl_3$)

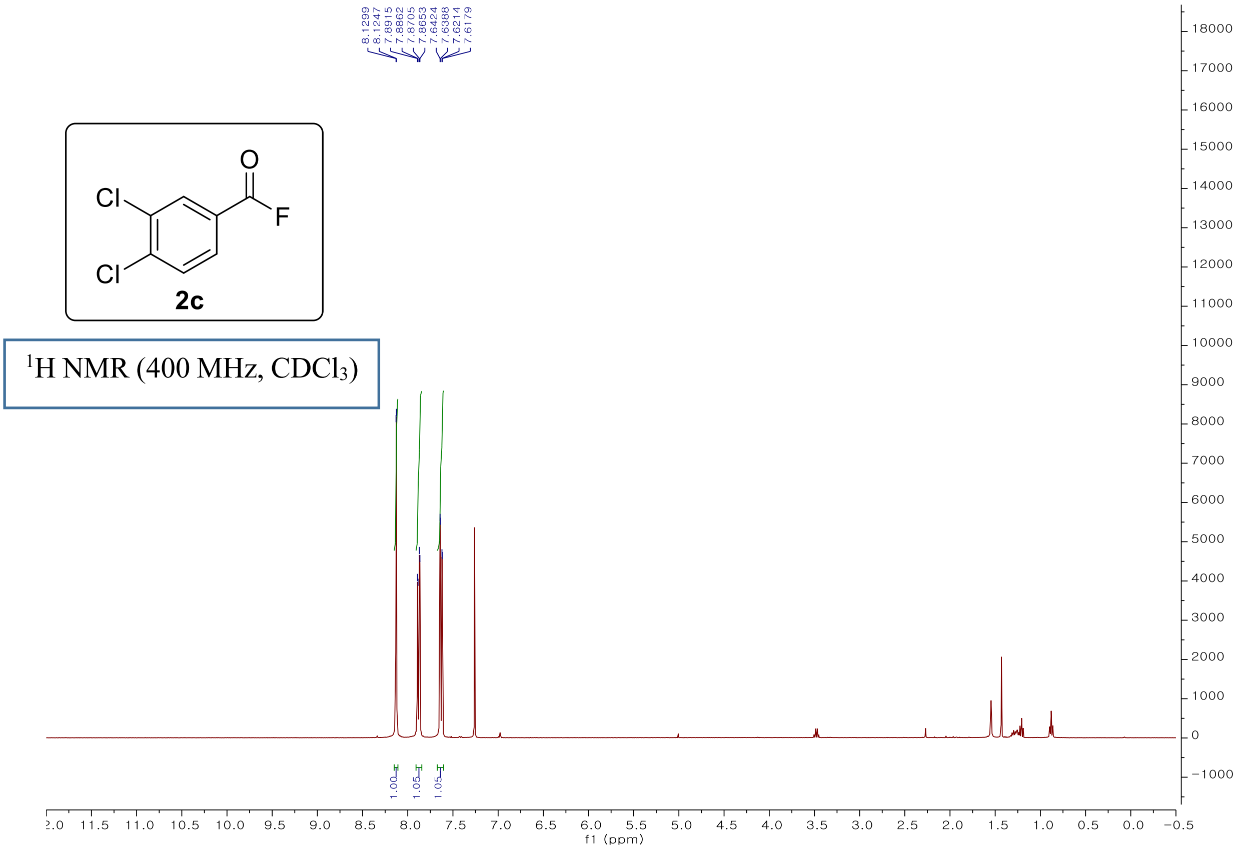

**2b**

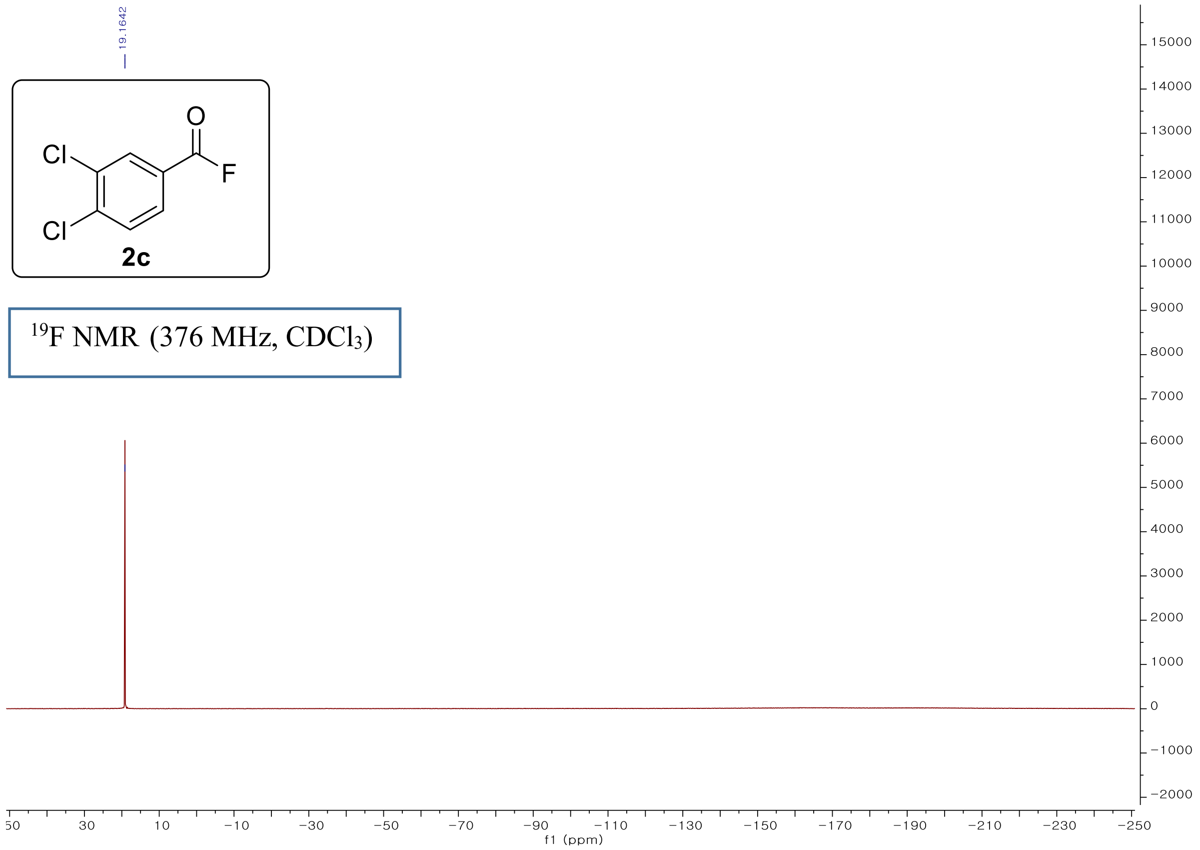
$^1$H NMR (500 MHz, CDCl$_3$)



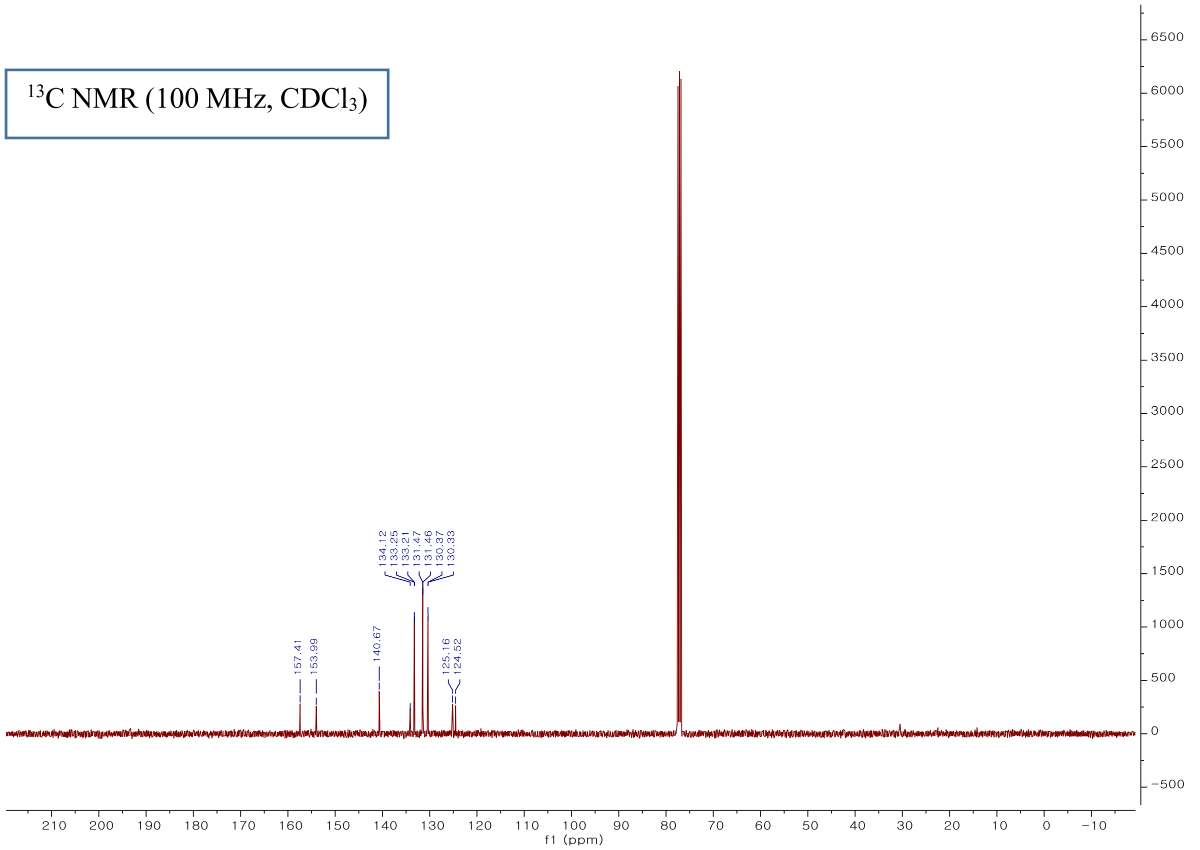
$^{19}$F NMR (376 MHz, CDCl$_3$)


Br
O
F
2b
$^{13}$C NMR (100 MHz, CDCl$_3$)
77.48
77.16
76.84
138.45
134.39
134.35
130.74
130.73
130.09
130.05
127.31
126.69
123.22
123.21
157.90
154.47
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

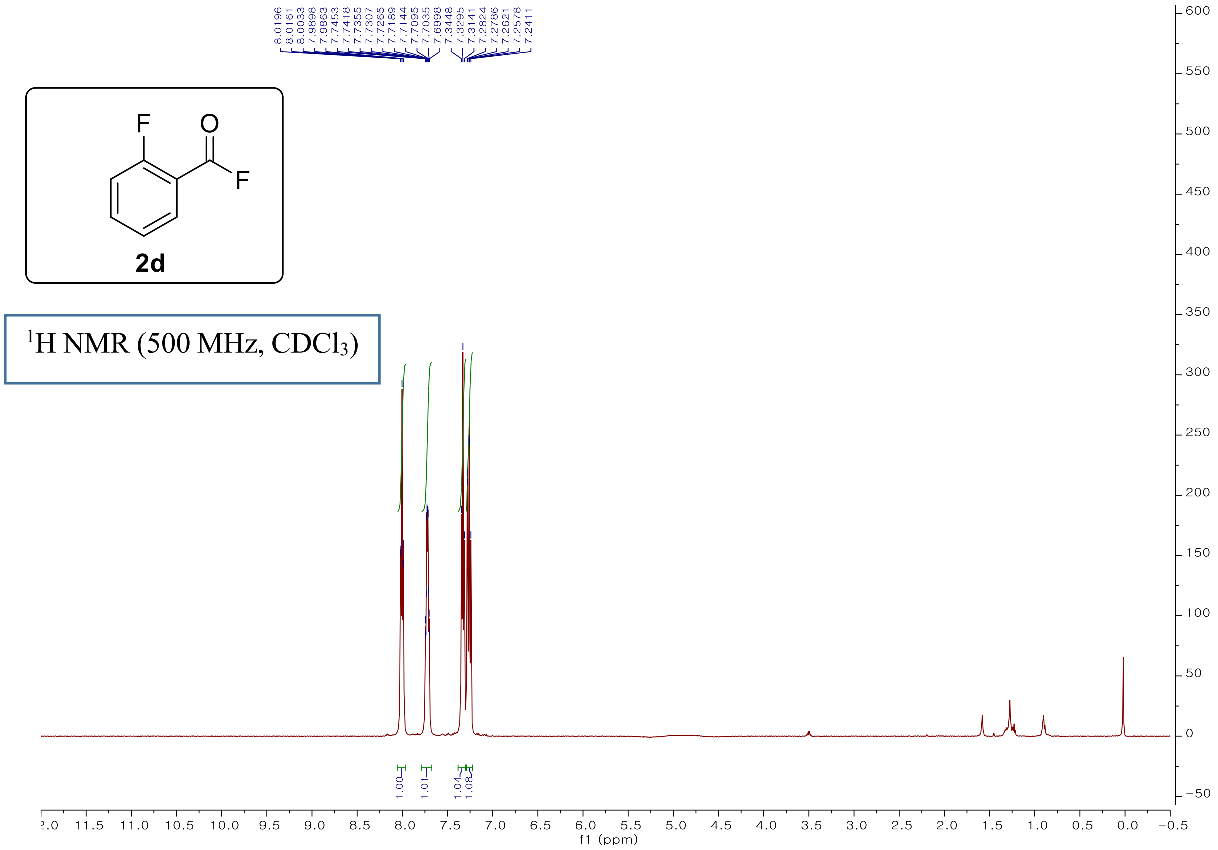

8.1299
8.1247
7.8915
7.8862
7.8705
7.8653
7.6424
7.6388
7.6214
7.6179
Cl
Cl
O
F
2c
$^{1}$H NMR (400 MHz, CDCl$_3$)
1.00
1.05
1.05
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)



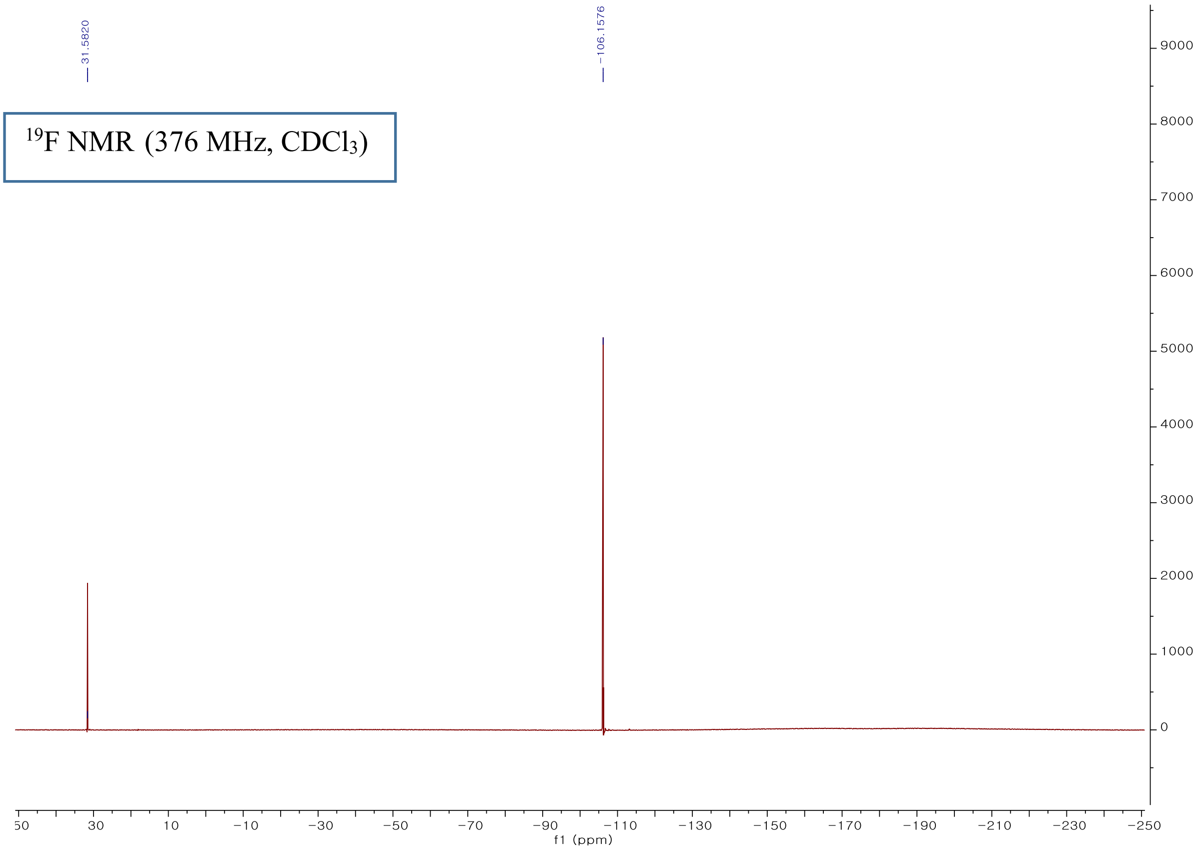
$^{19}$F NMR (376 MHz, CDCl$_3$)



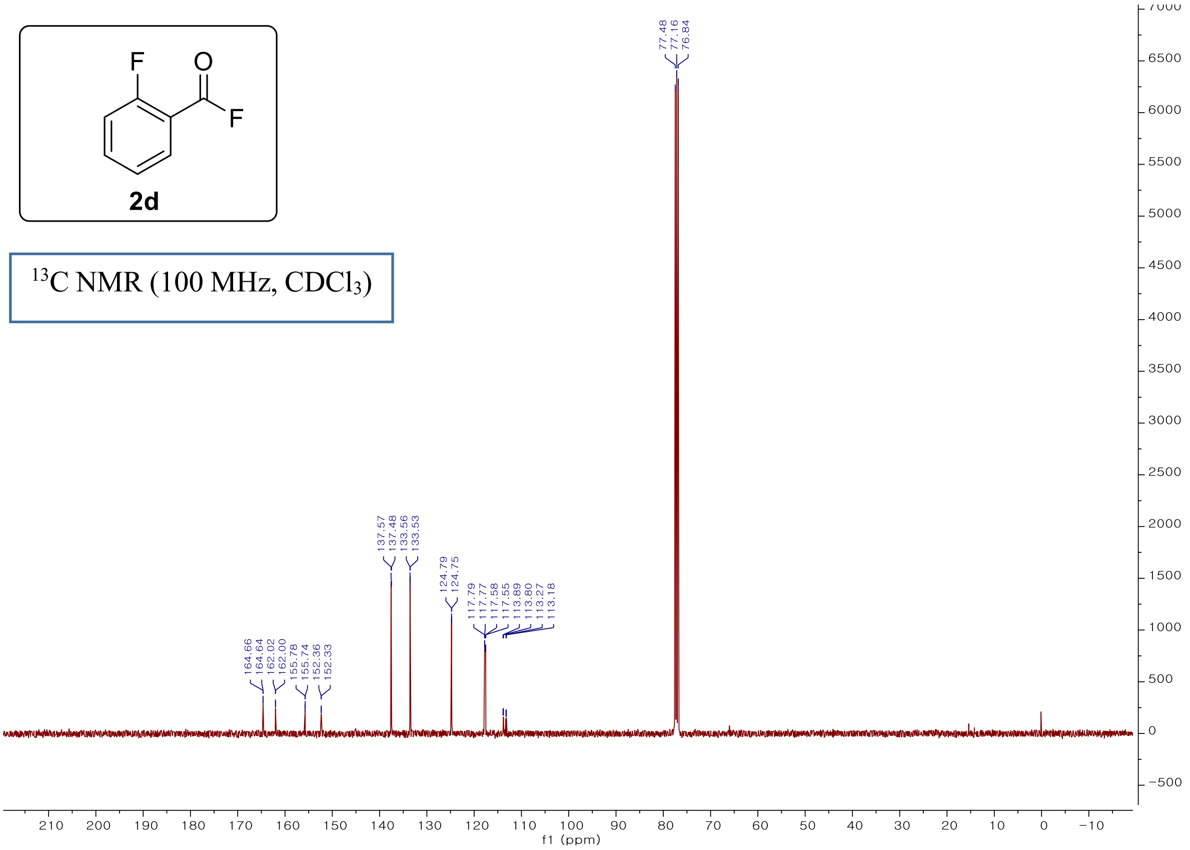
$^{13}$C NMR (100 MHz, CDCl$_3$)



$^1$H NMR (500 MHz, CDCl$_3$)

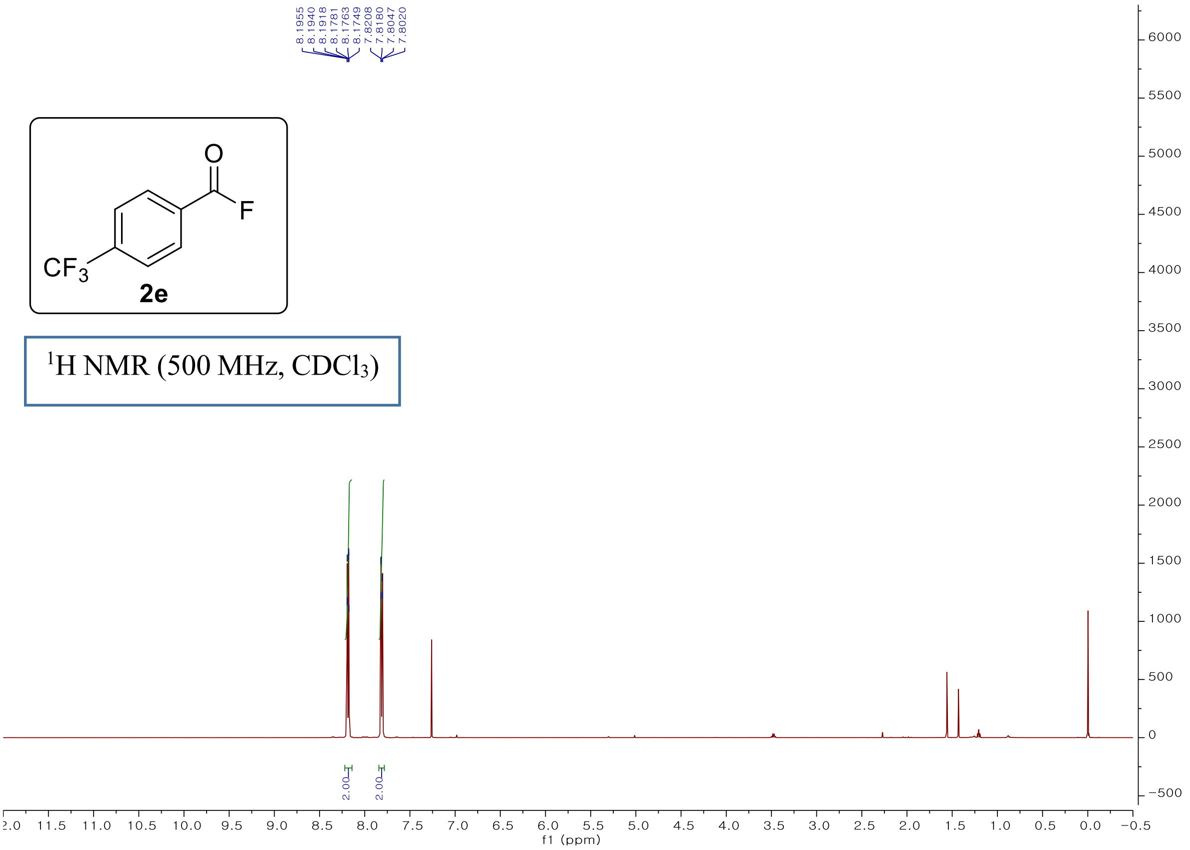


$^{19}$F NMR (376 MHz, CDCl$_3$)



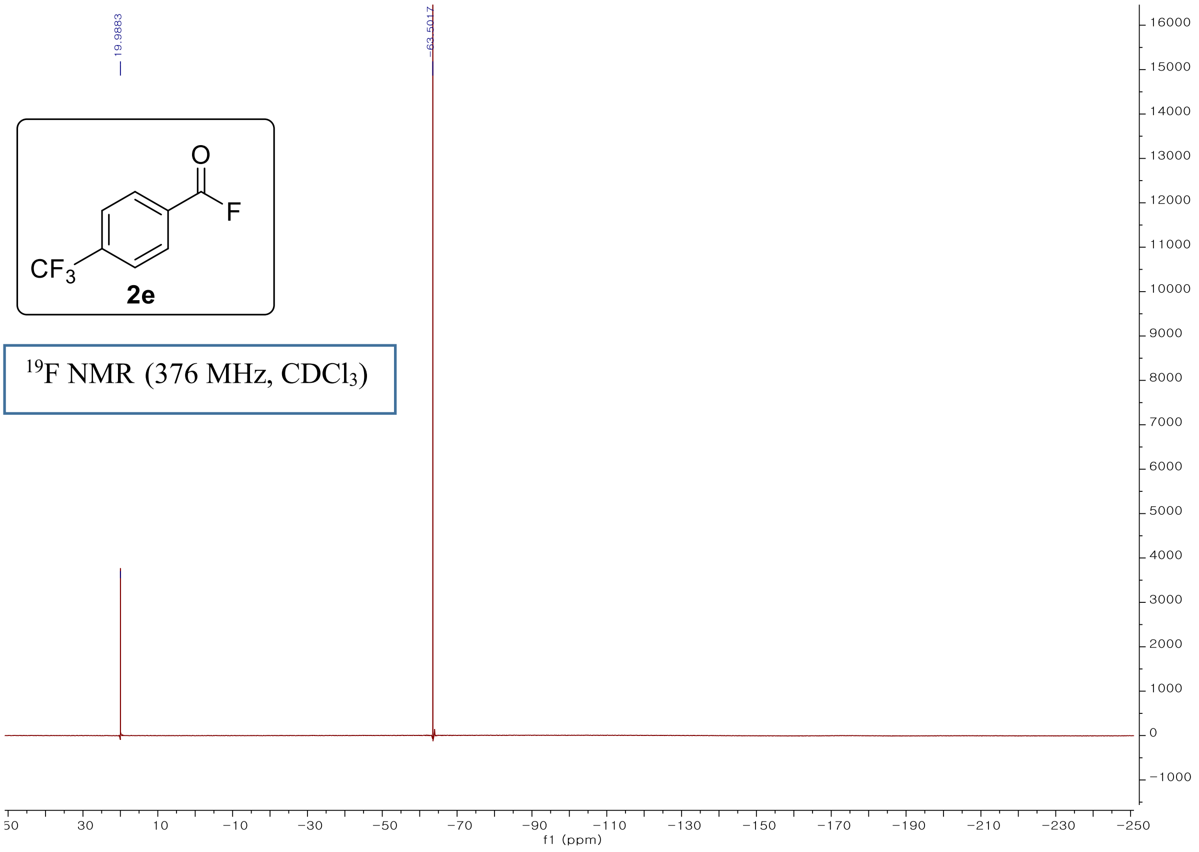
**2d**

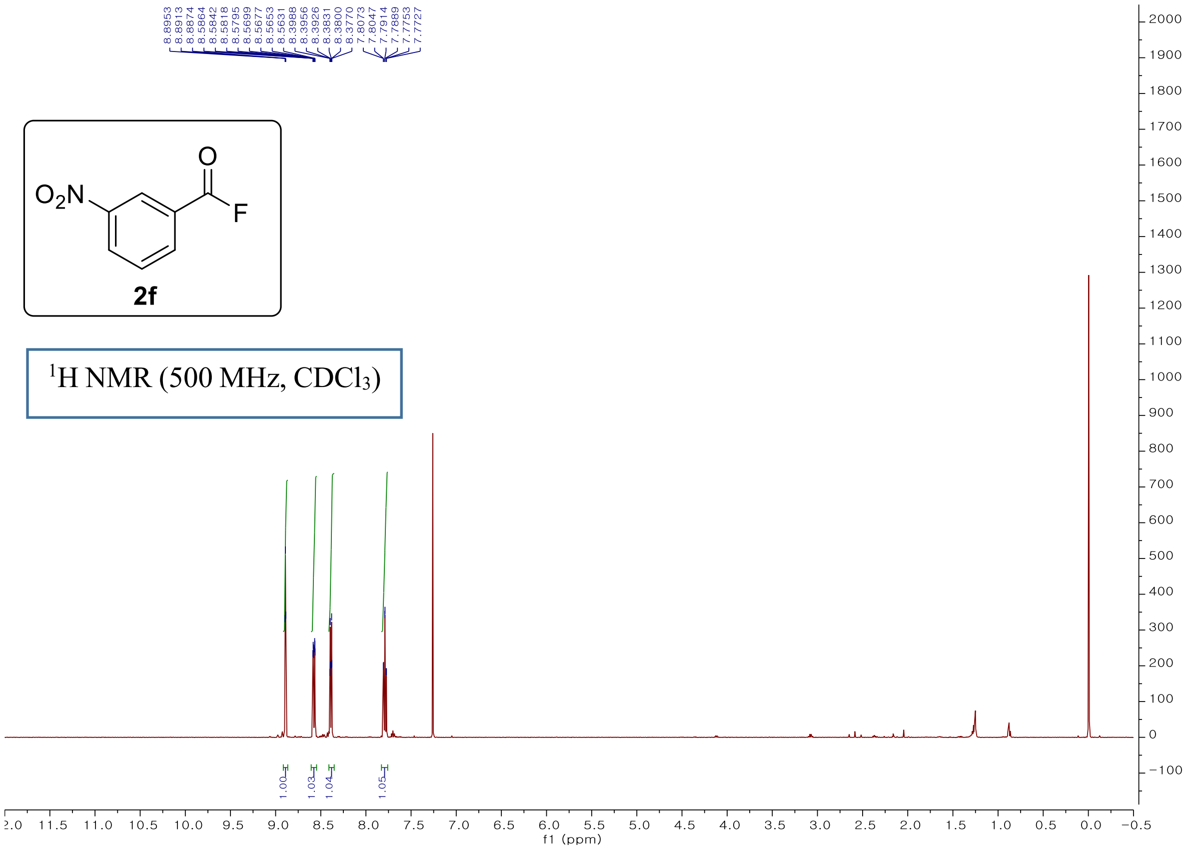
$^{13}$C NMR (100 MHz, CDCl$_3$)

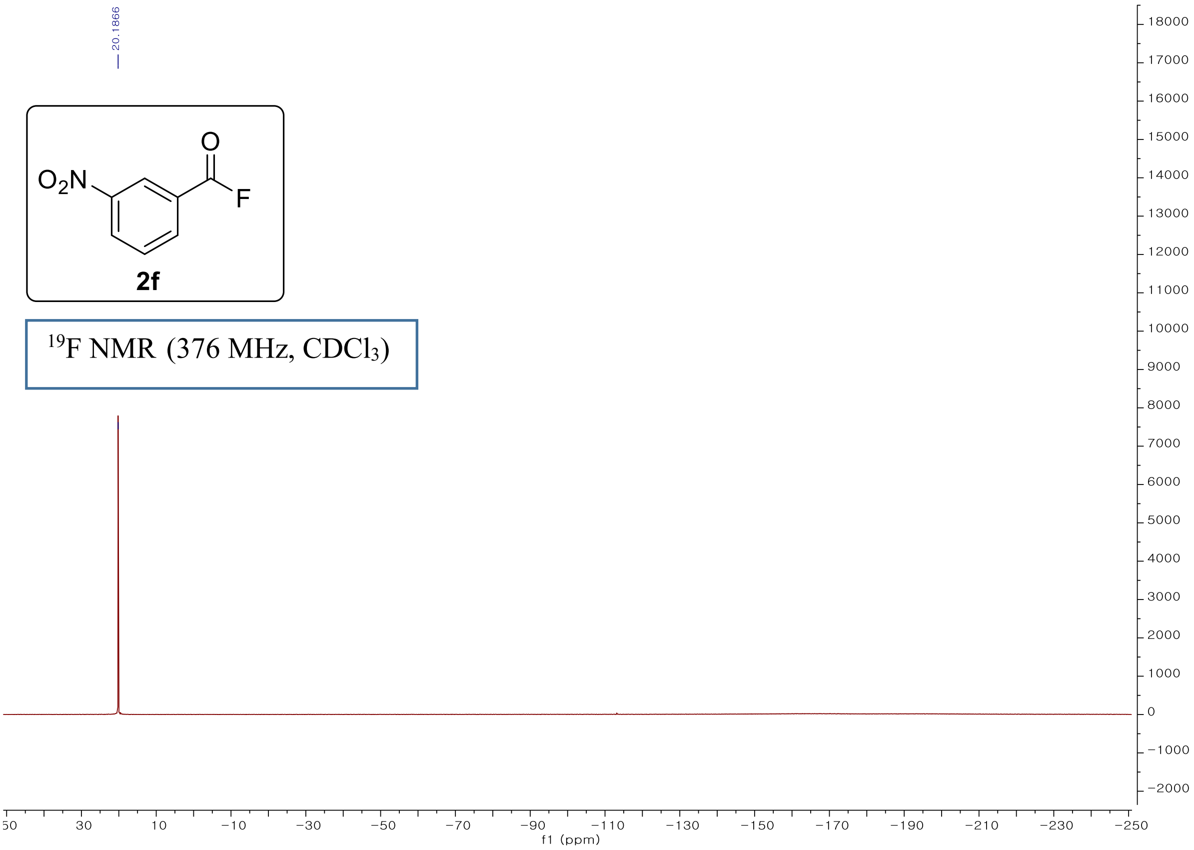


**2e**

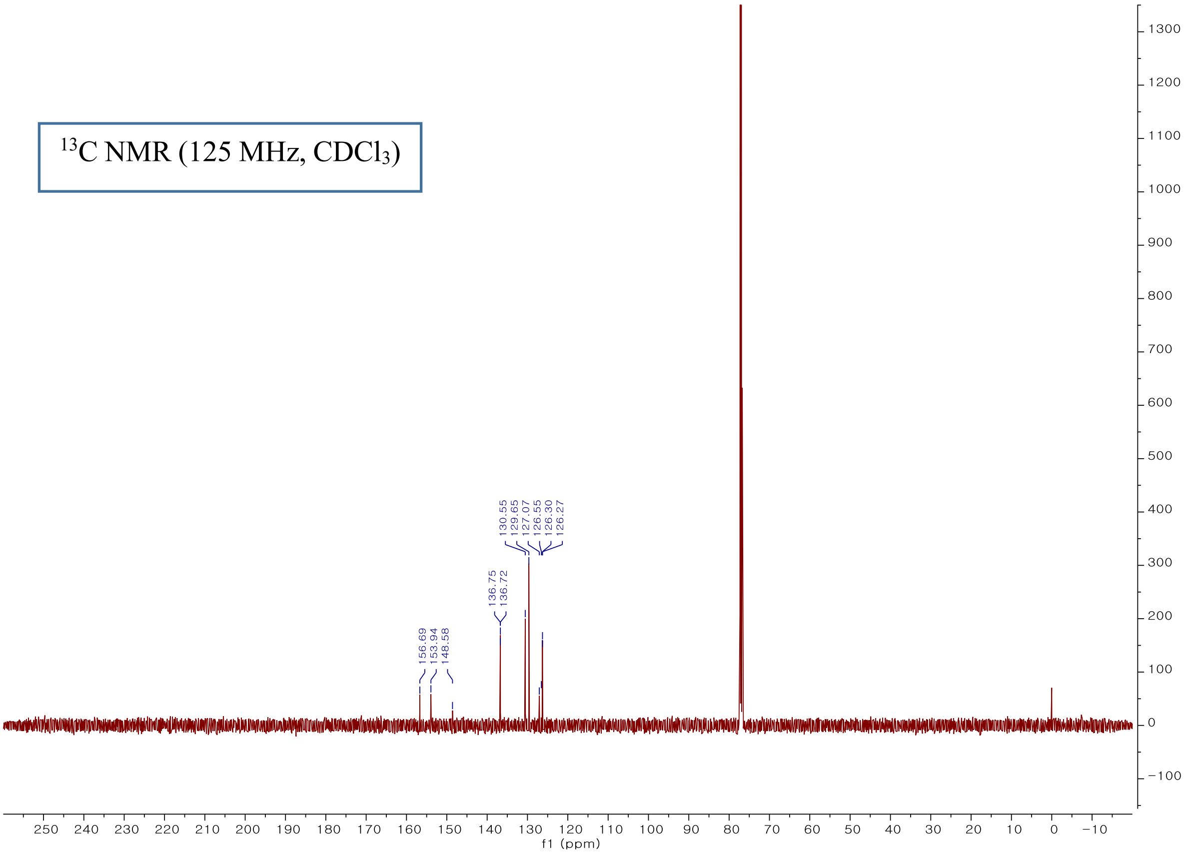
$^1$H NMR (500 MHz, CDCl$_3$)


19.9883
-63.5017
CF3
O
F
2e
19F NMR (376 MHz, CDCl3)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

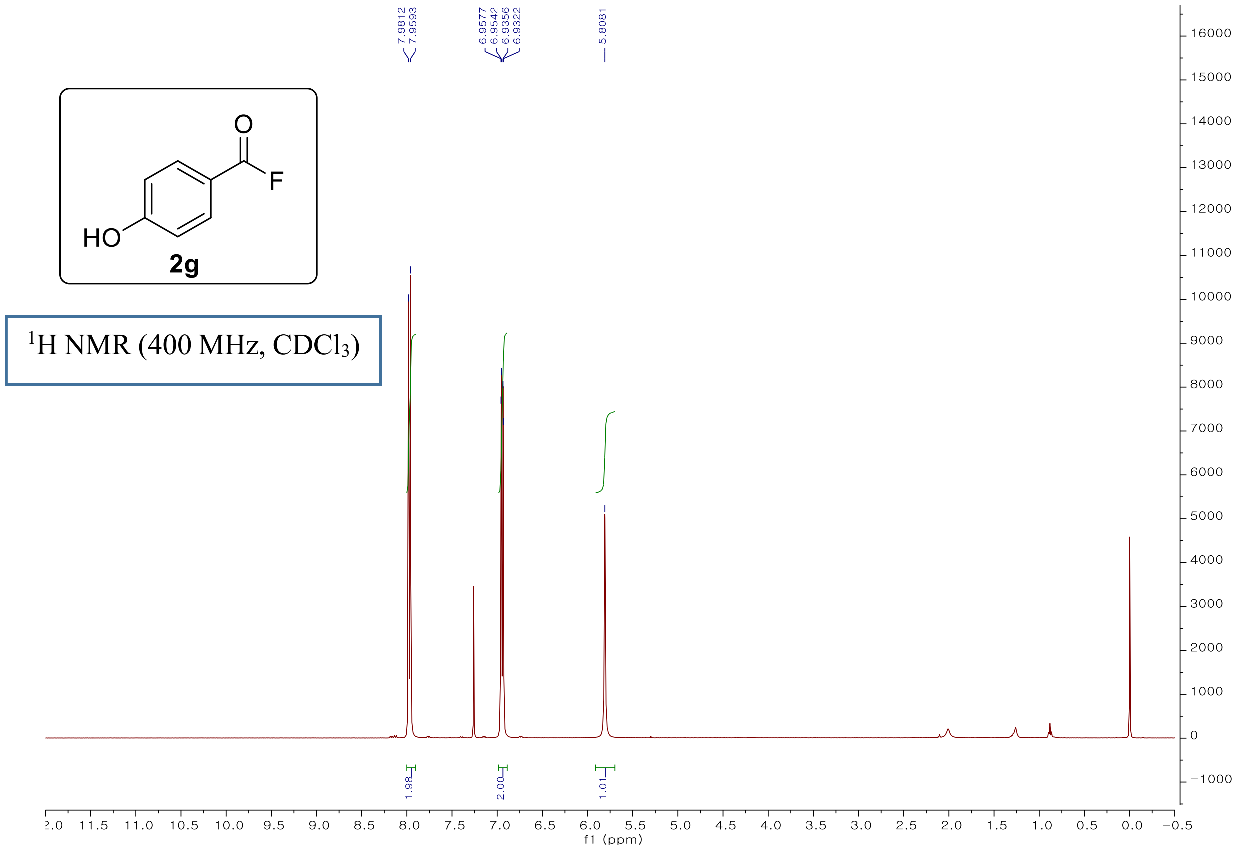

8.8953
8.8913
8.8874
8.5864
8.5842
8.5818
8.5795
8.5699
8.5677
8.5653
8.5631
8.3988
8.3956
8.3926
8.3831
8.3800
8.3770
7.8073
7.8047
7.7914
7.7889
7.7753
7.7727
O2N
O
F
2f
1H NMR (500 MHz, CDCl3)
1.00
1.03
1.04
1.05
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



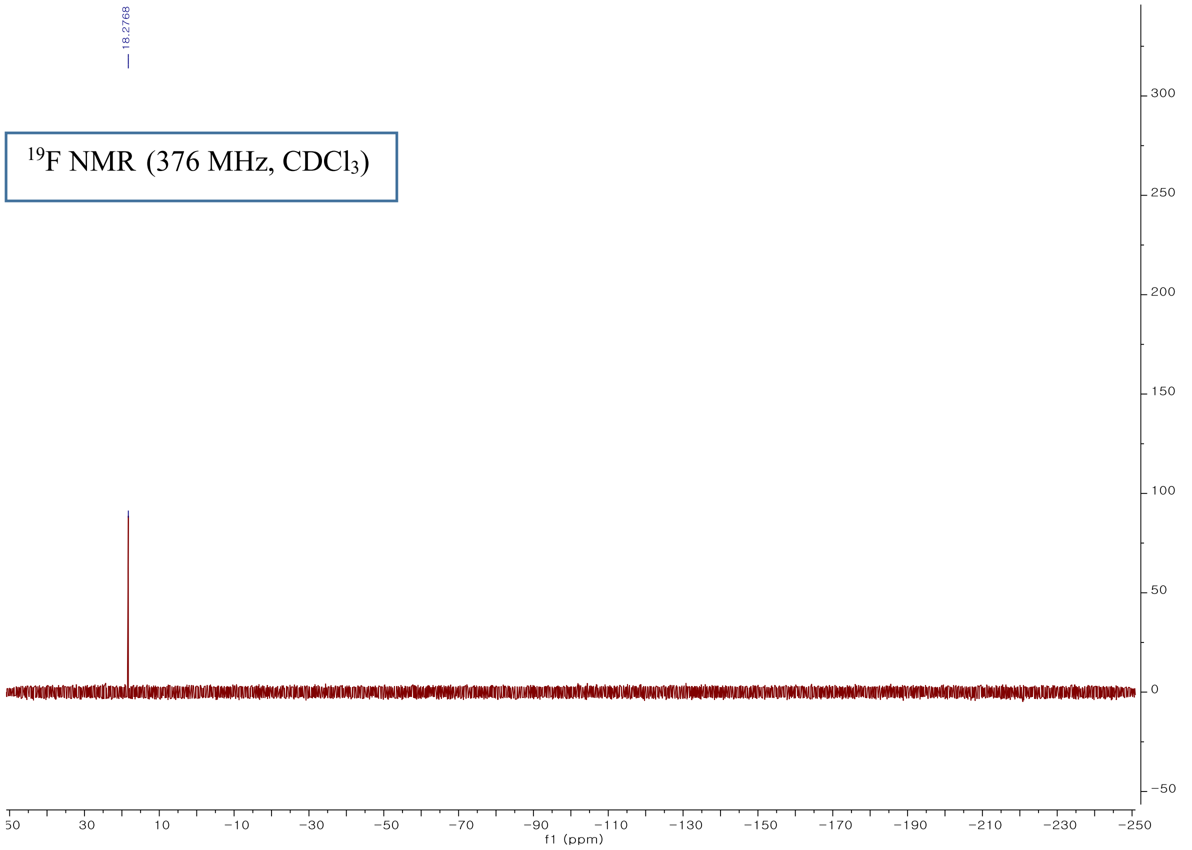
$^{19}$F NMR (376 MHz, $CDCl_3$)



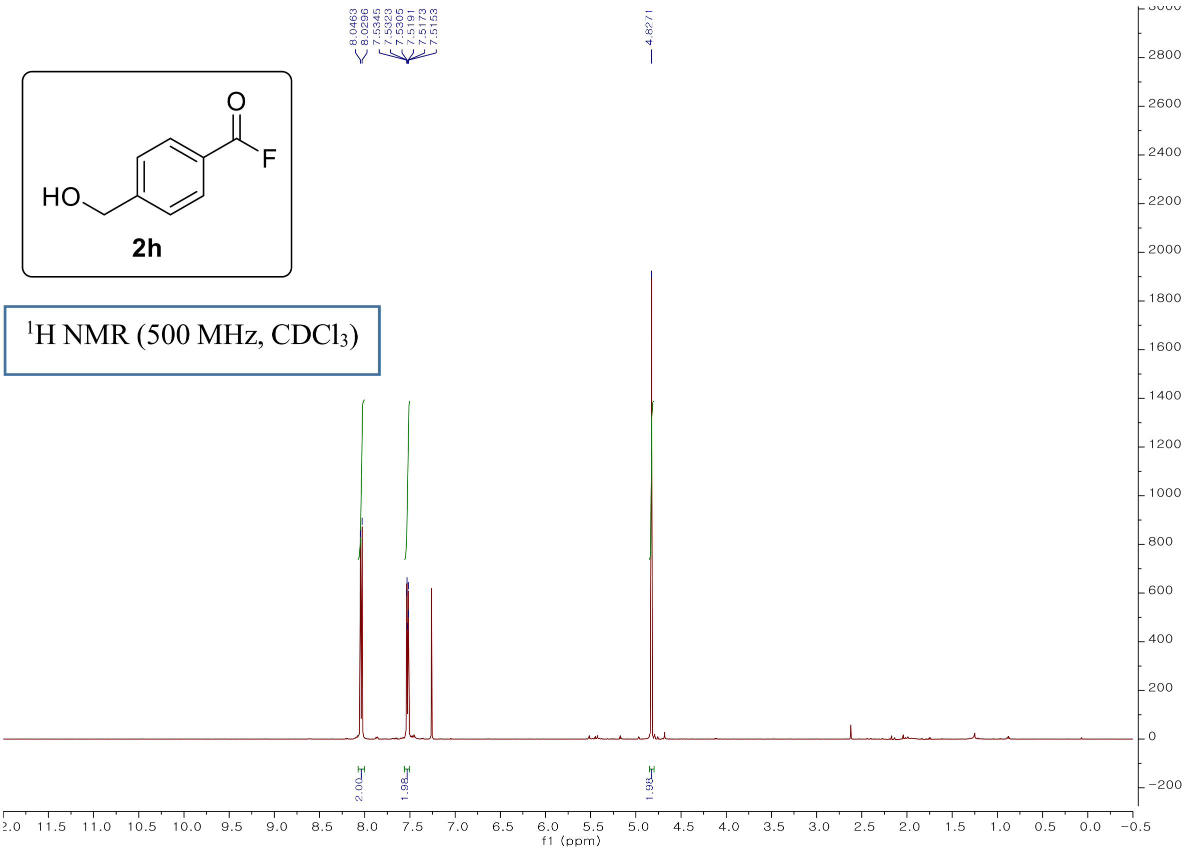
$^{13}$C NMR (125 MHz, $CDCl_3$)



$^1$H NMR (400 MHz, CDCl$_3$)

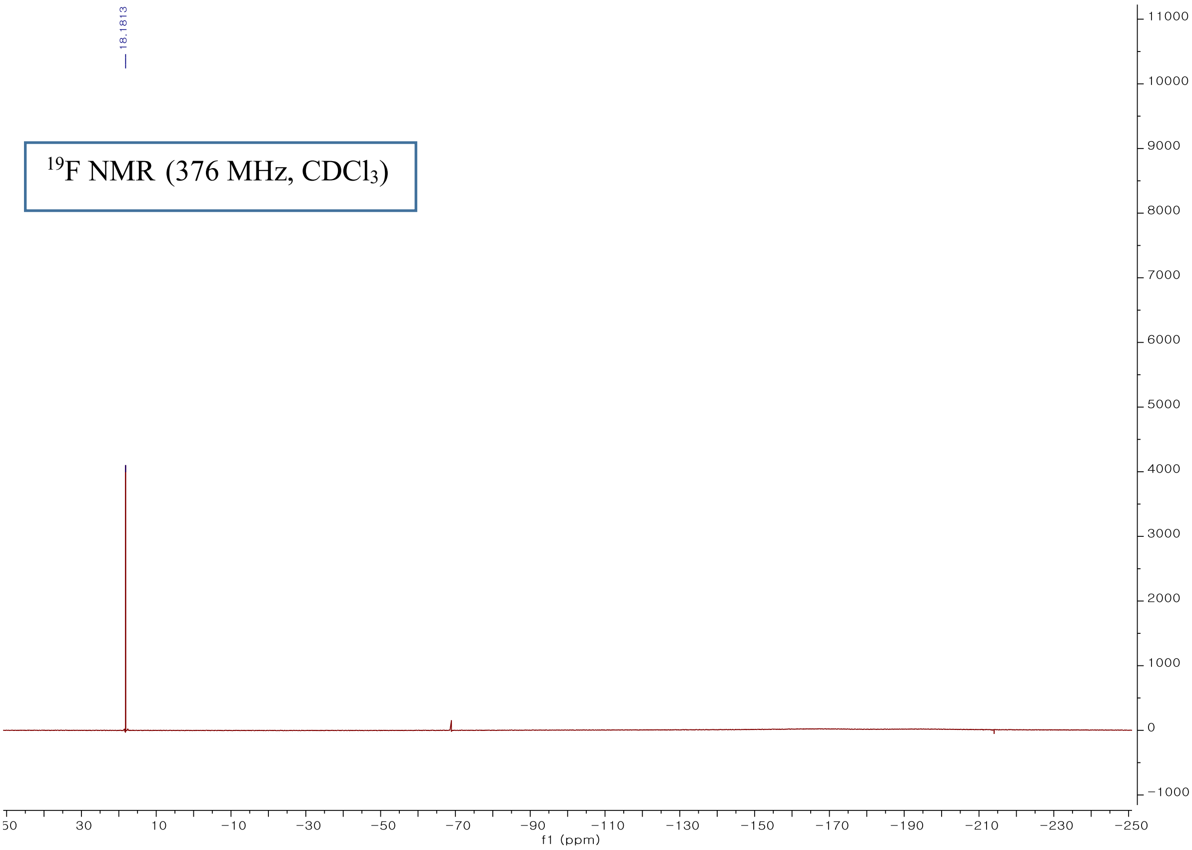


$^{19}$F NMR (376 MHz, CDCl$_3$)

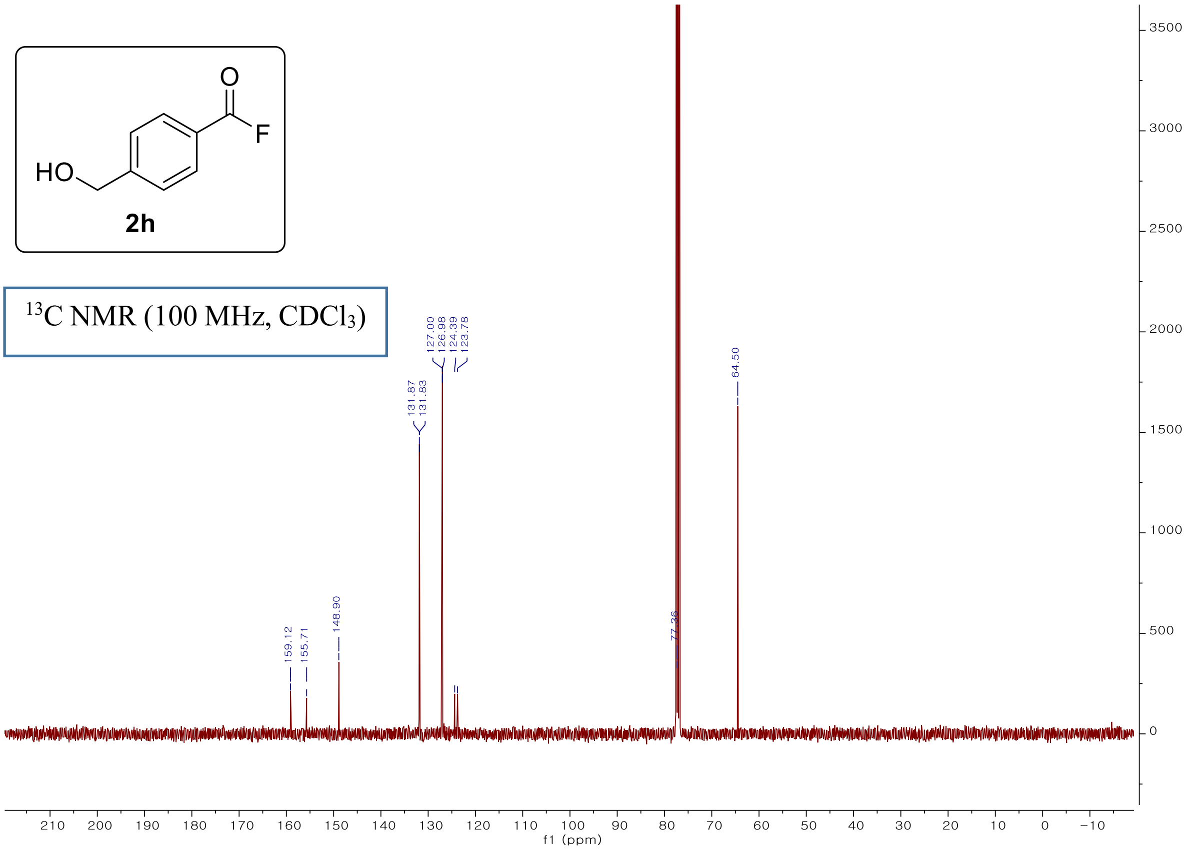


**2h**

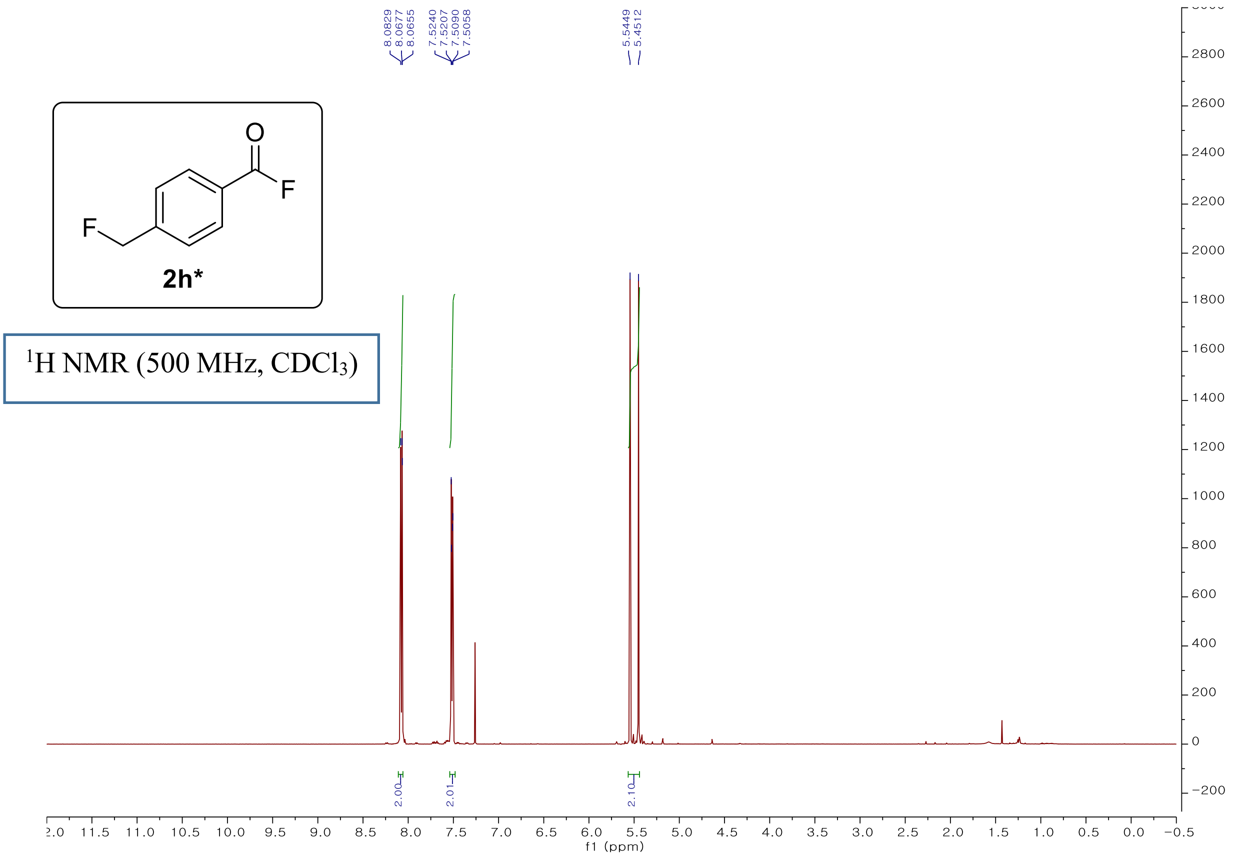
$^{1}$H NMR (500 MHz, CDCl$_3$)



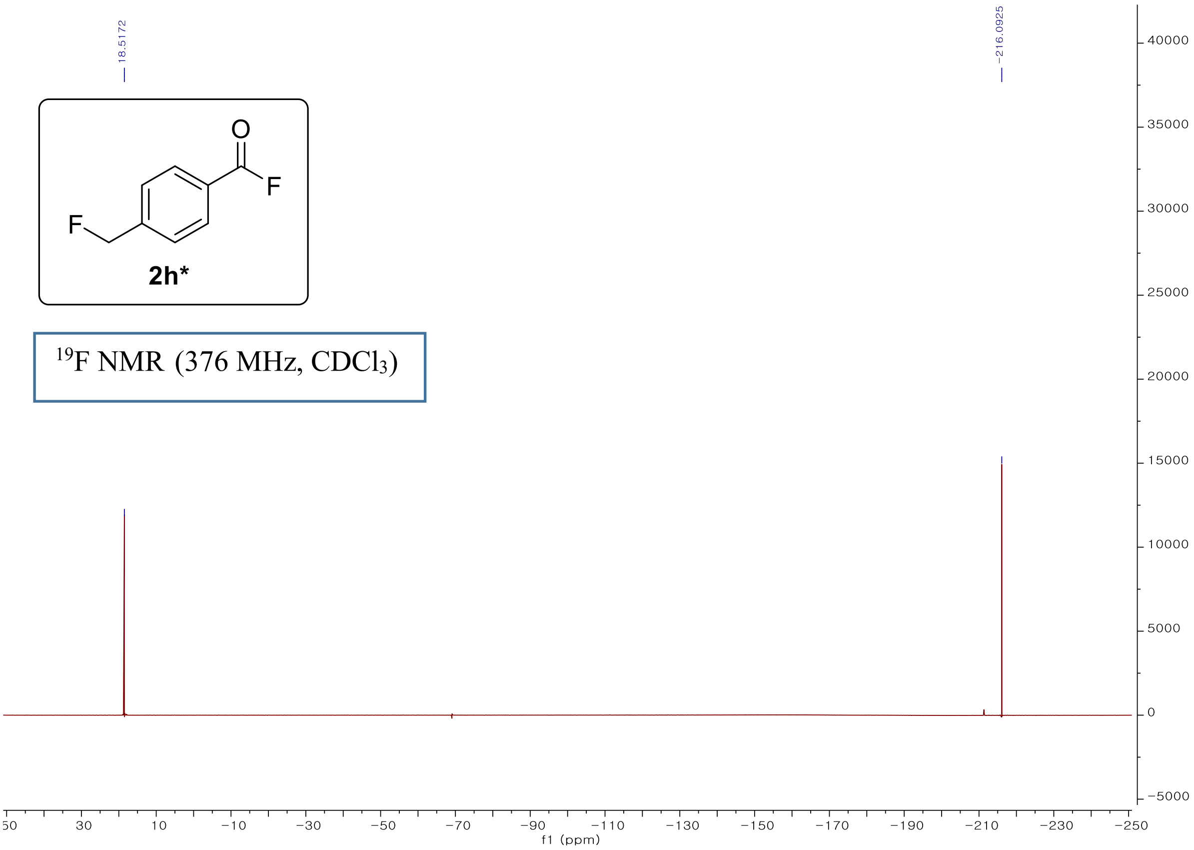
$^{19}$F NMR (376 MHz, CDCl$_3$)

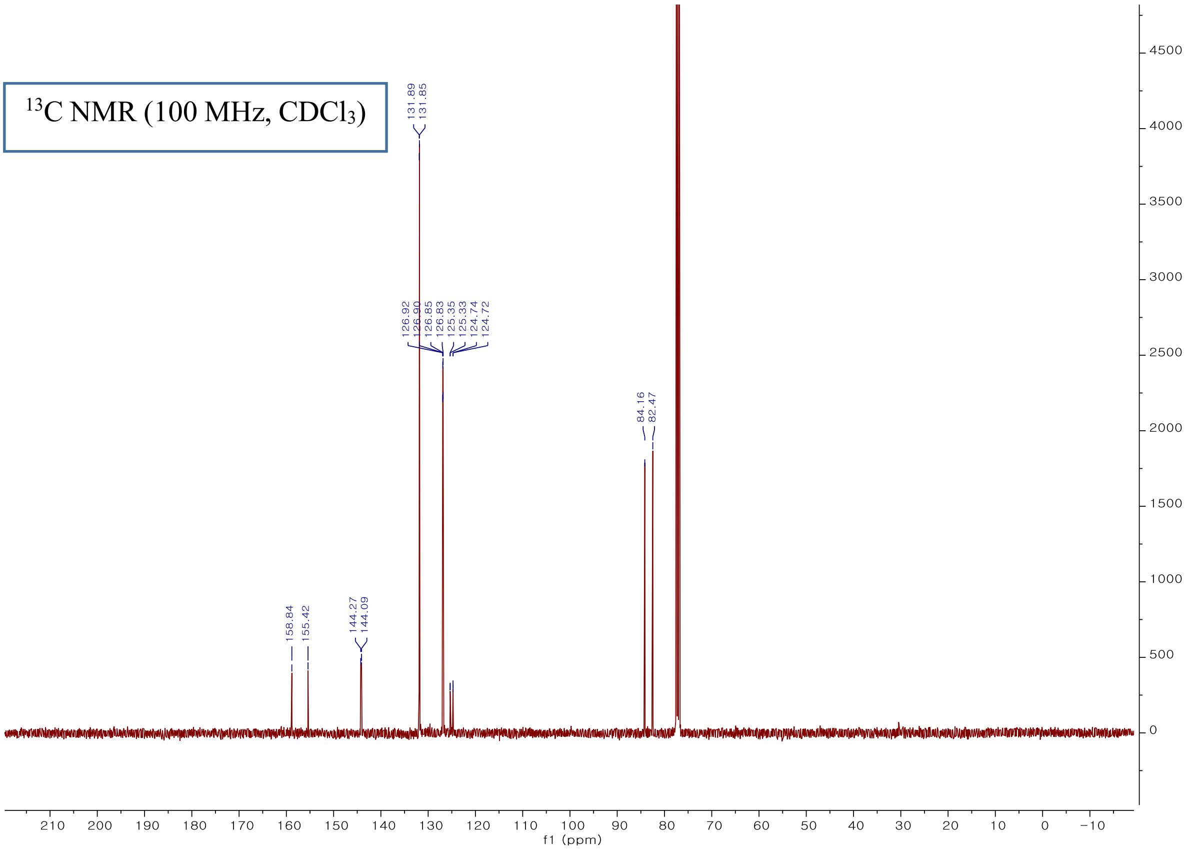


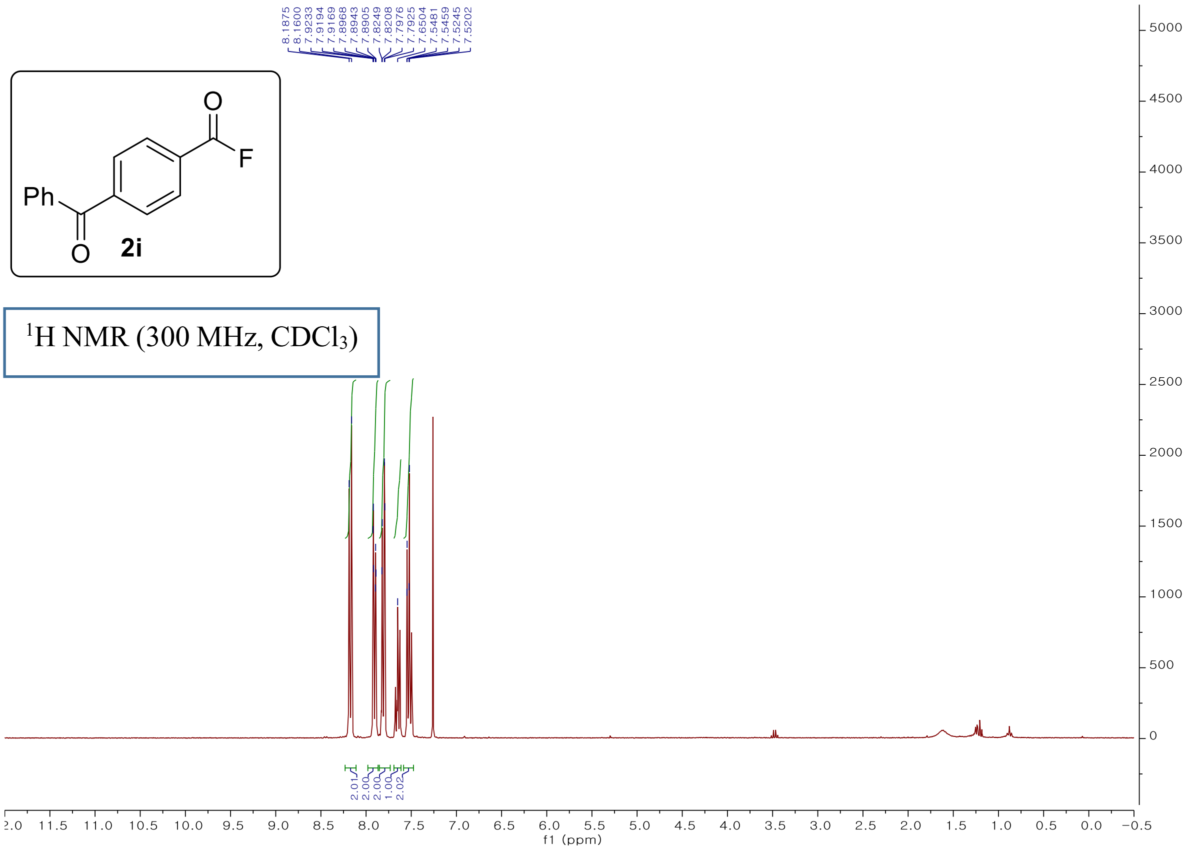
O
F
HO
2h
13C NMR (100 MHz, CDCl3)
159.12
155.71
148.90
131.87
131.83
127.00
126.98
124.39
123.78
77.36
64.50
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



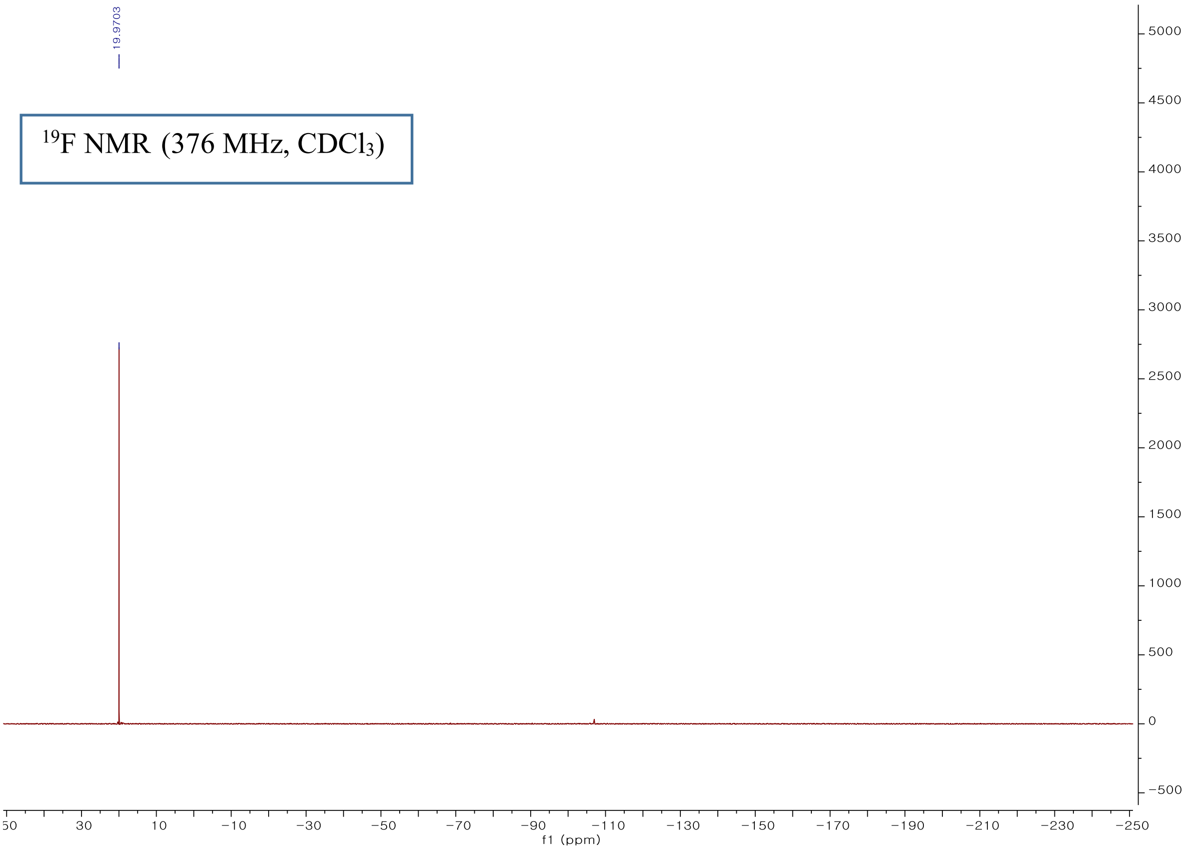
8.0829
8.0677
8.0655
7.5240
7.5207
7.5090
7.5058
5.5449
5.4512
O
F
F
2h*
1H NMR (500 MHz, CDCl3)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
2.00
2.01
2.10
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

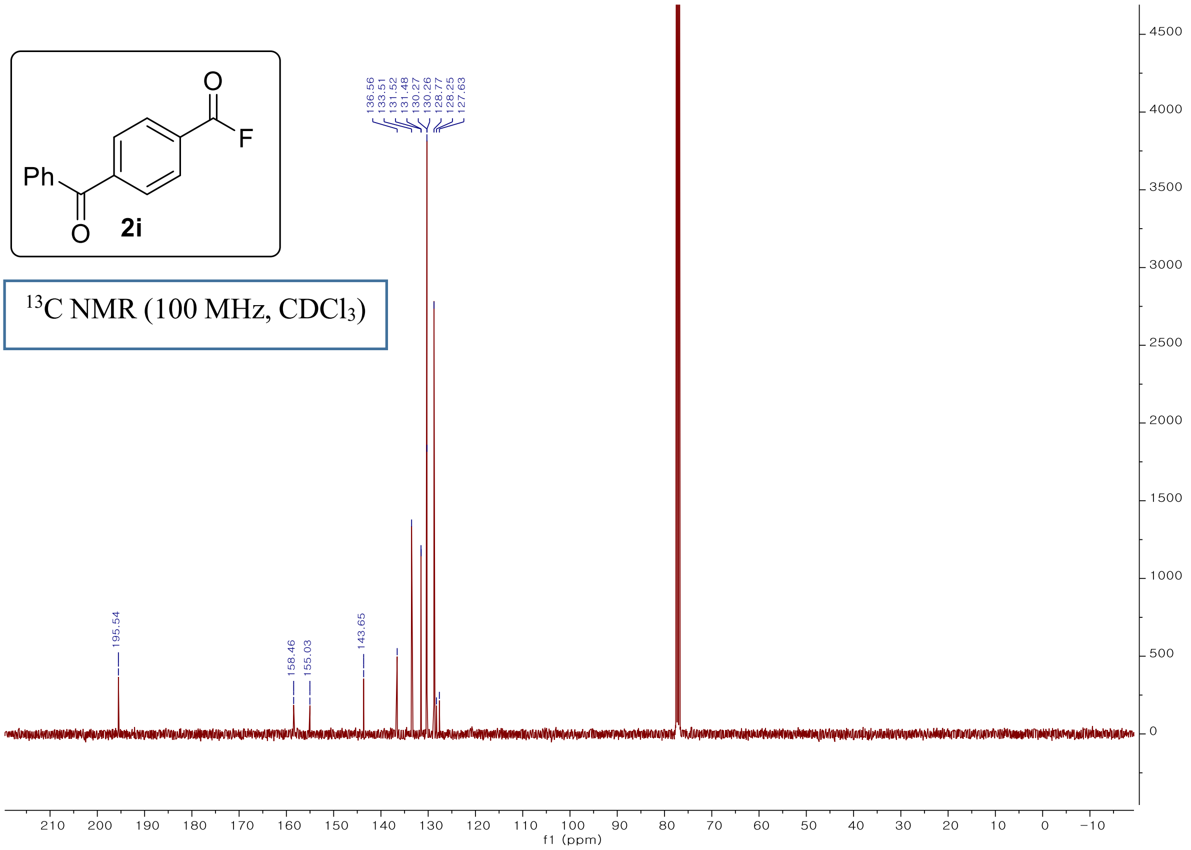

18.5172
-216.0925
2h*
$^{19}$F NMR (376 MHz, CDCl$_3$)
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−250
f1 (ppm)


$^{13}$C NMR (100 MHz, CDCl$_3$)
131.89
131.85
126.92
126.90
126.85
126.83
125.35
125.33
124.74
124.72
84.16
82.47
158.84
155.42
144.27
144.09
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


**2i**

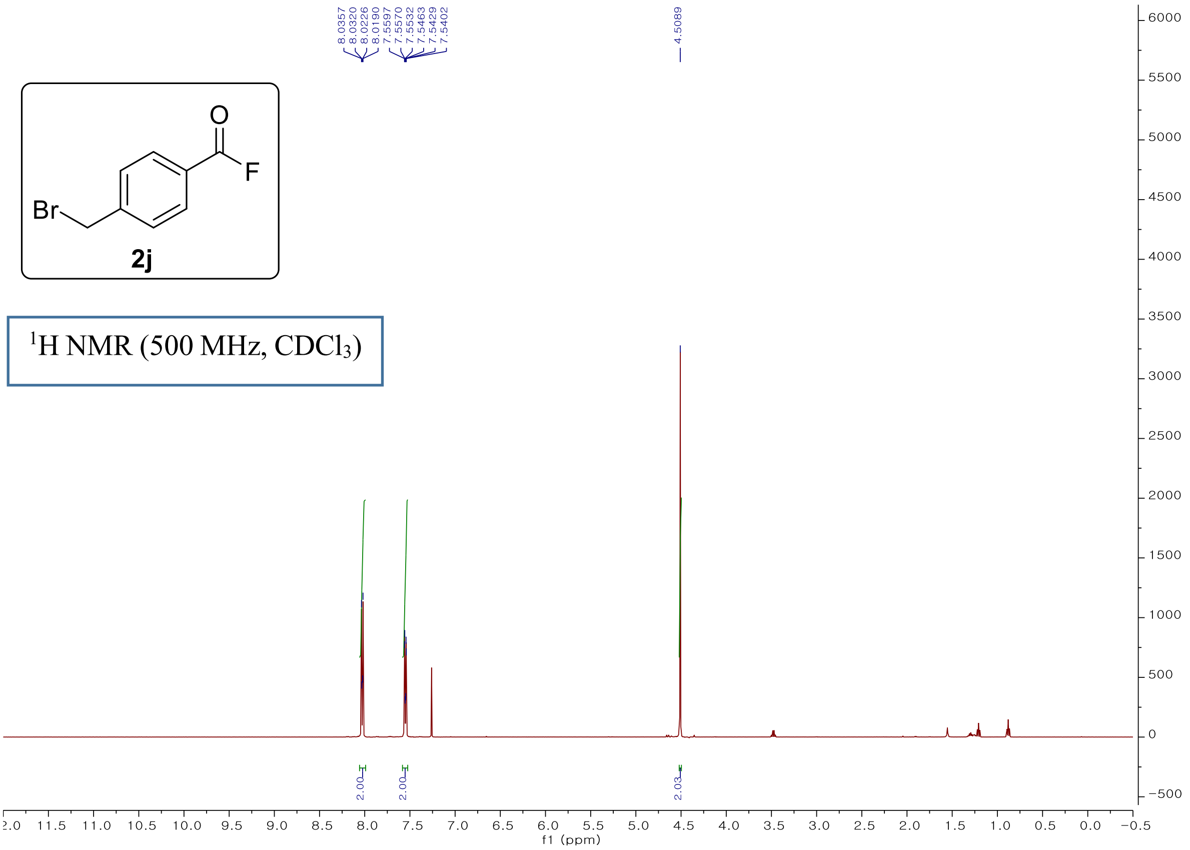
$^1$H NMR (300 MHz, CDCl$_3$)


$^{19}$F NMR (376 MHz, CDCl$_3$)



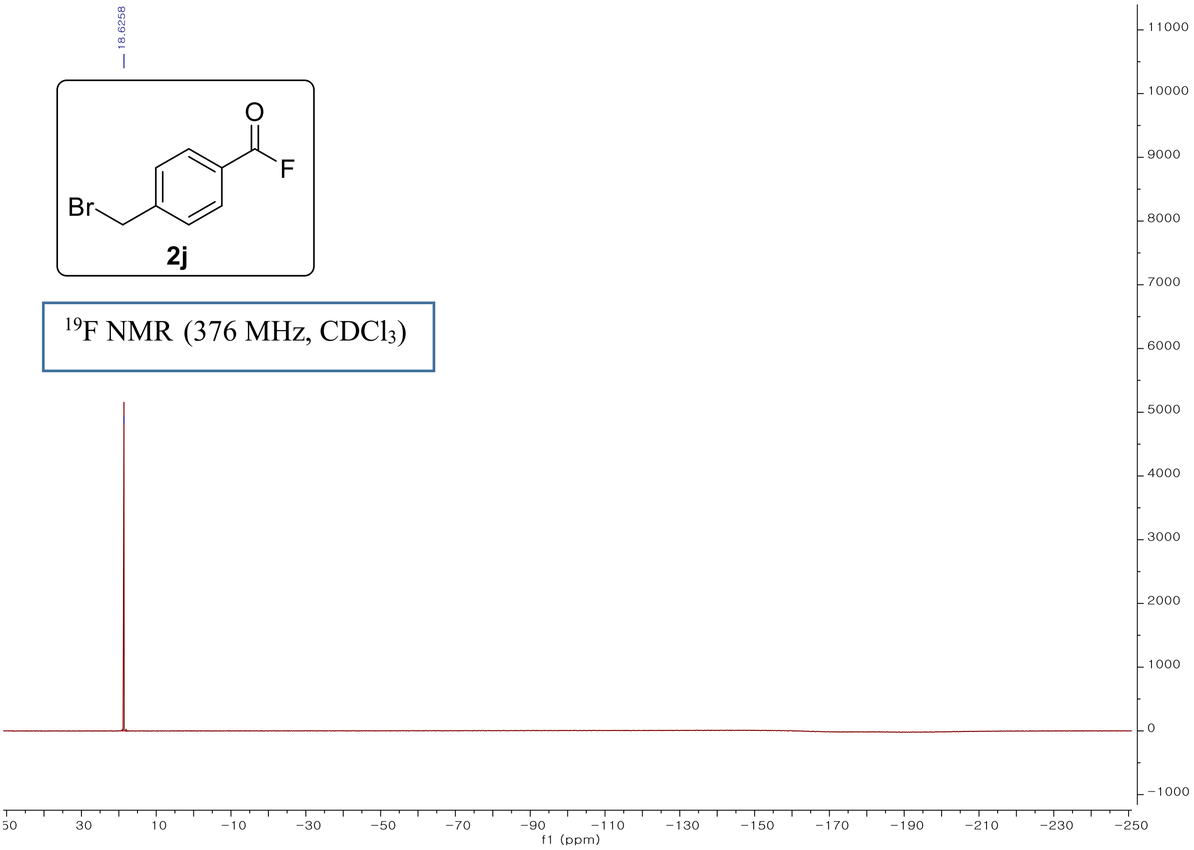
**2i**

$^{13}$C NMR (100 MHz, $CDCl_3$)

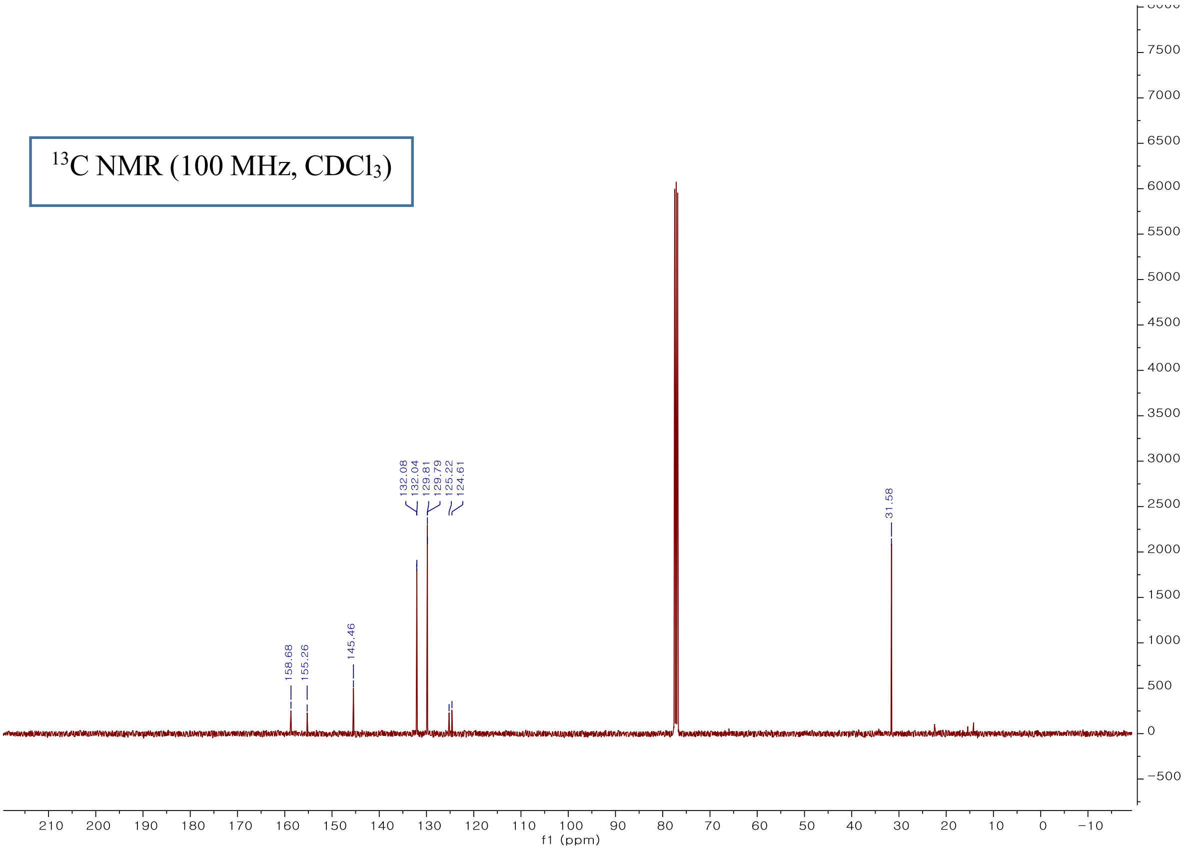


**2j**

$^{1}$H NMR (500 MHz, $CDCl_3$)



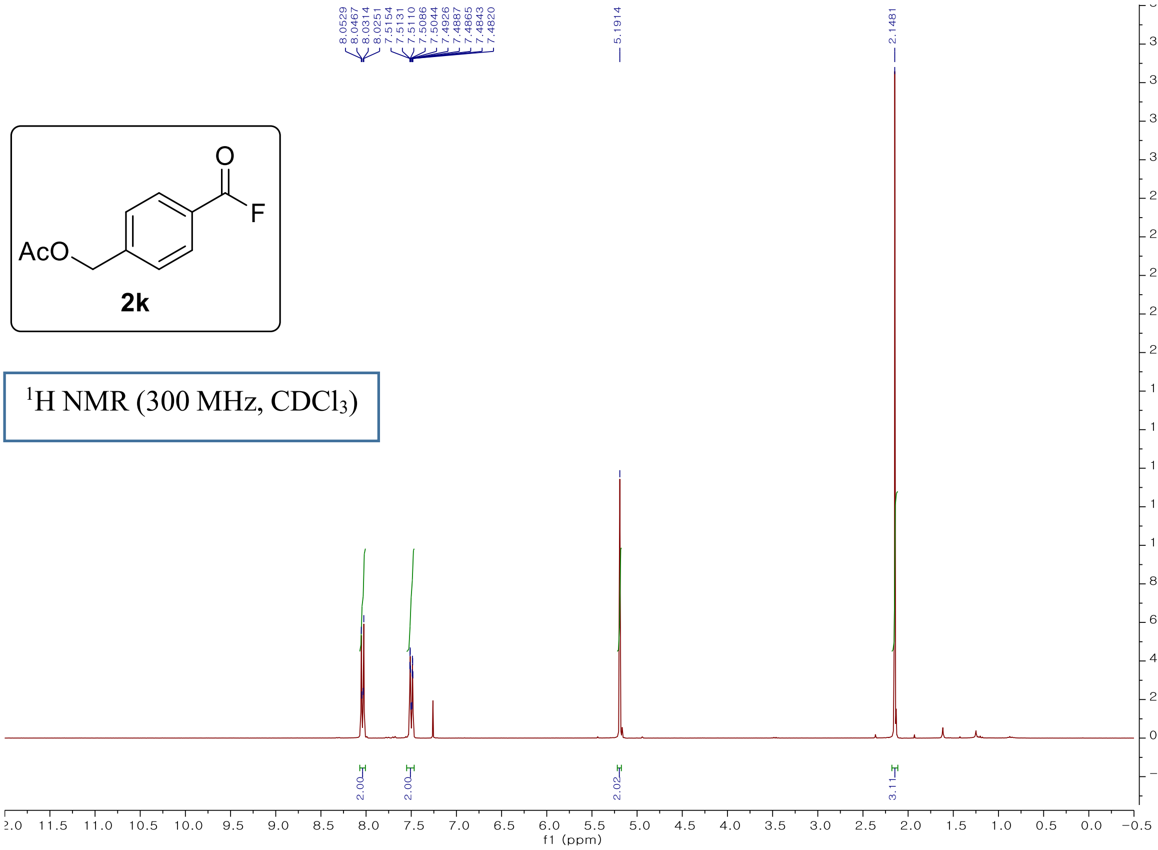
$^{19}F$ NMR (376 MHz, $CDCl_3$)



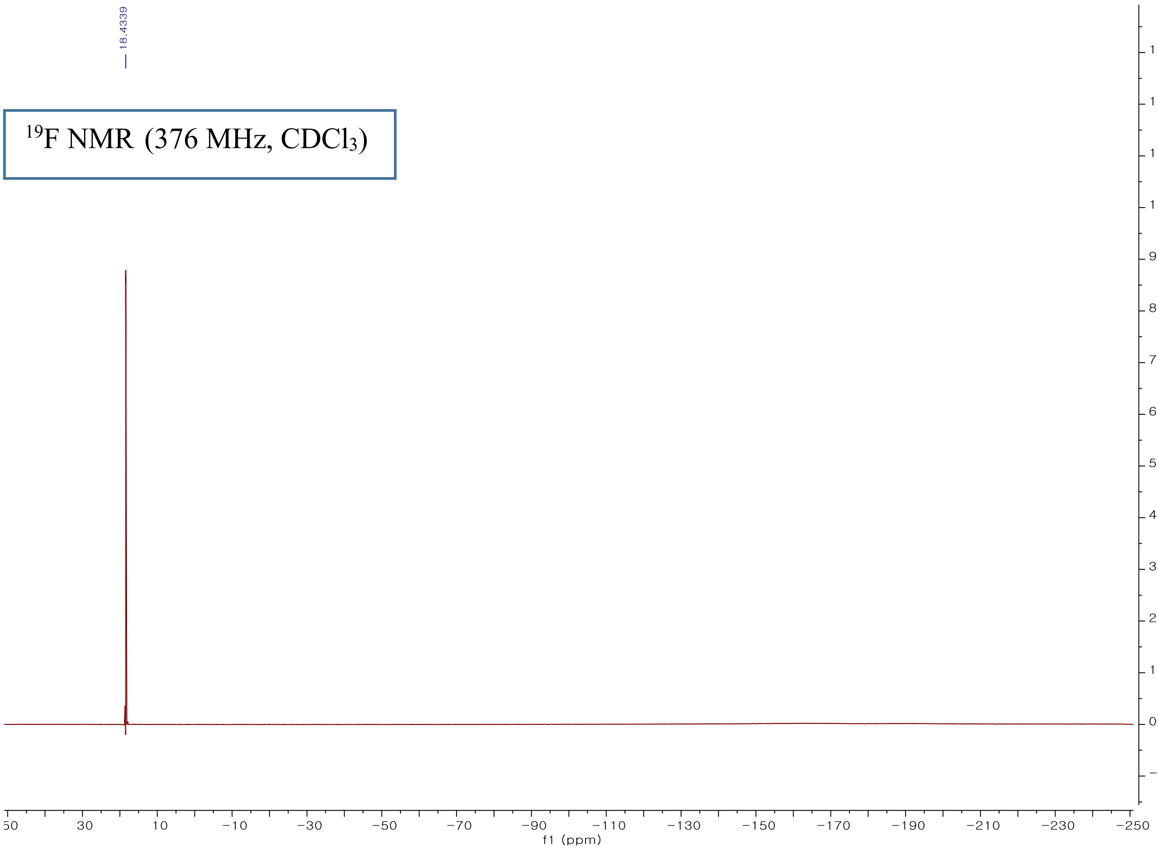
$^{13}C$ NMR (100 MHz, $CDCl_3$)

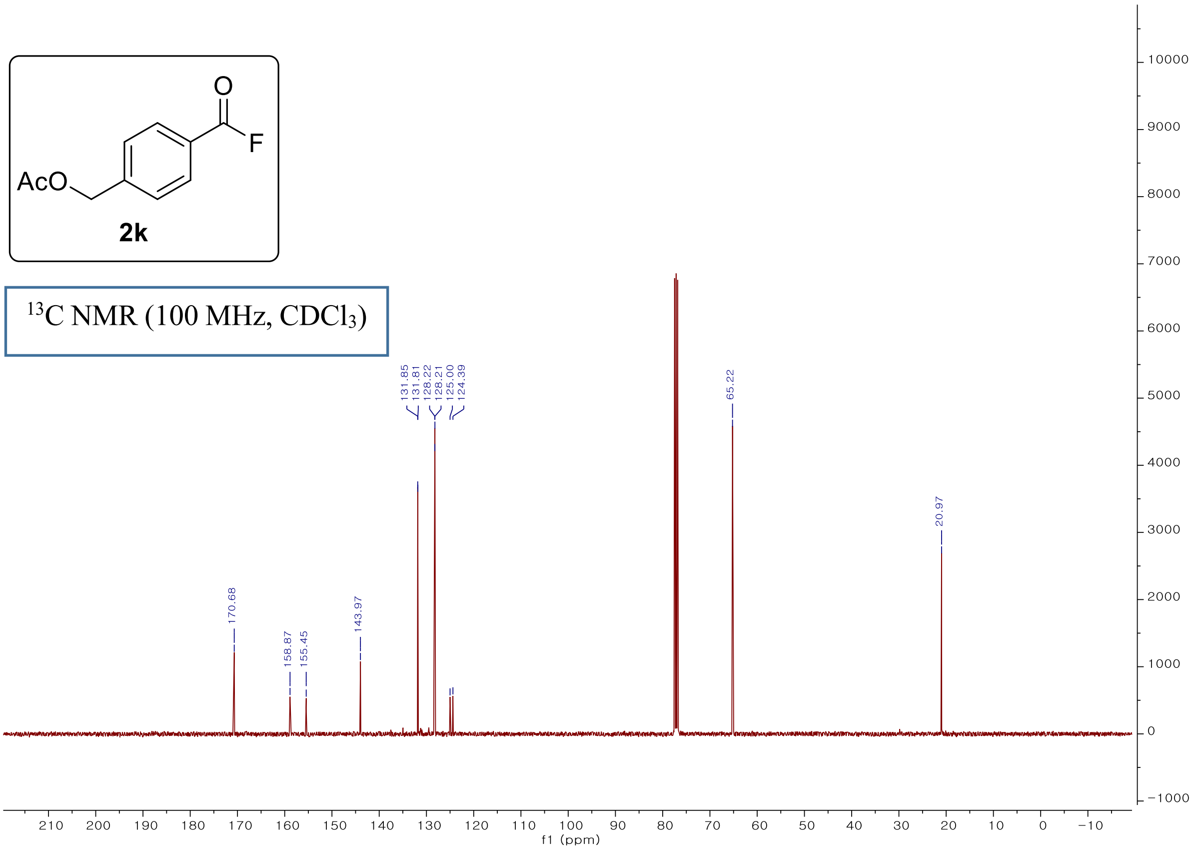
**2k**

$^1$H NMR (300 MHz, CDCl$_3$)



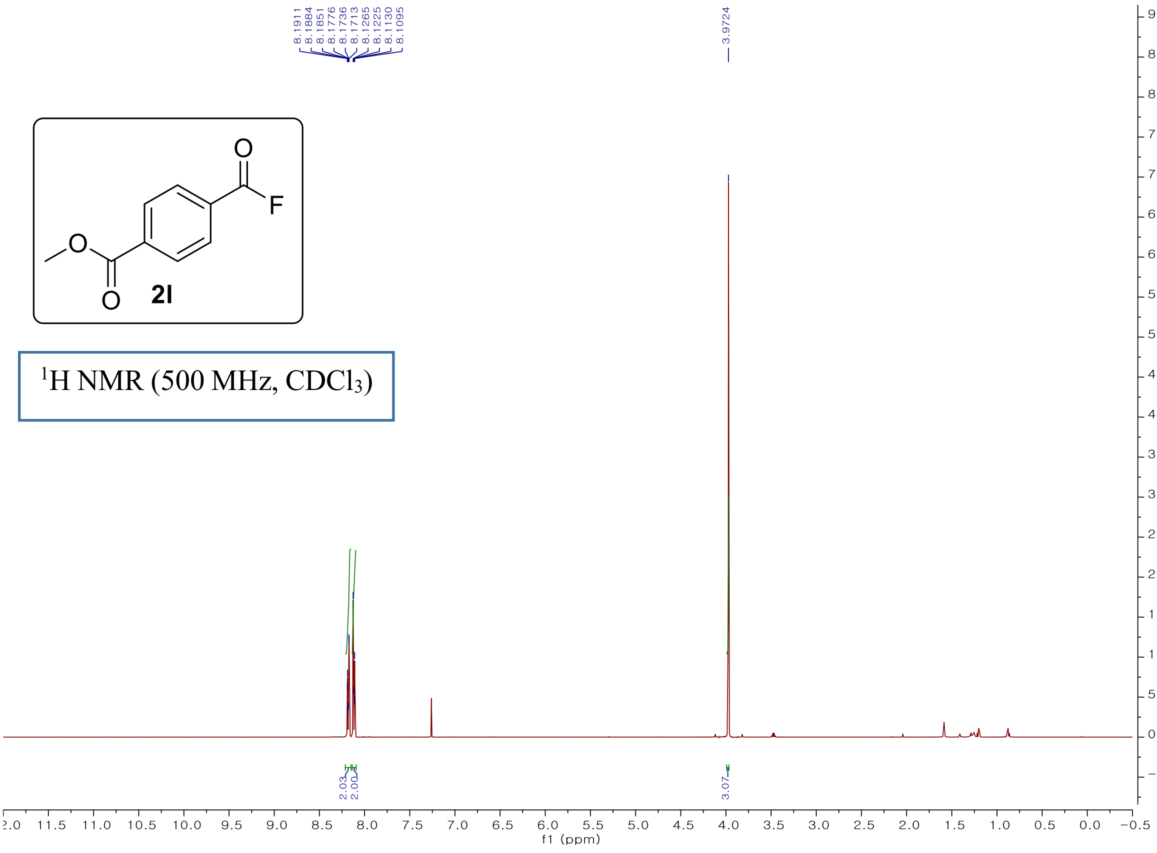
$^{19}$F NMR (376 MHz, CDCl$_3$)





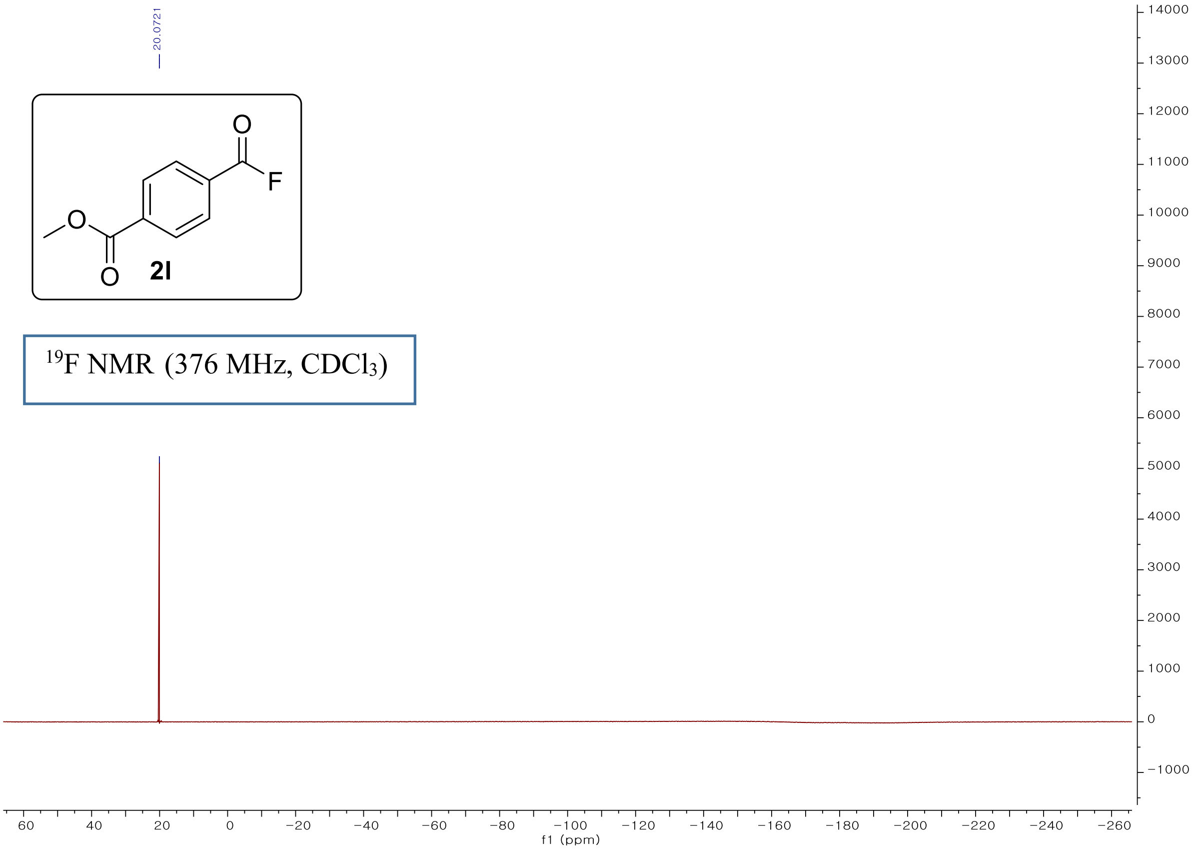
**2k**

$^{13}$C NMR (100 MHz, CDCl$_3$)

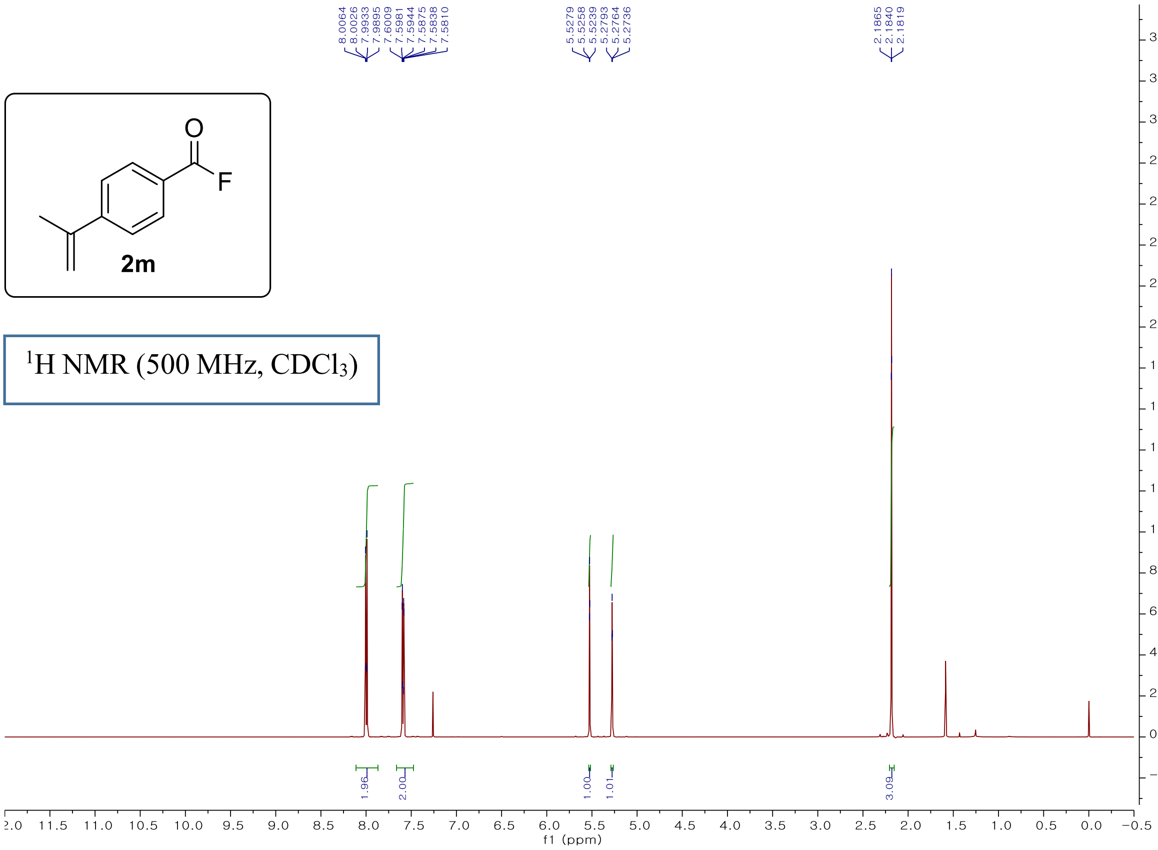


**2l**

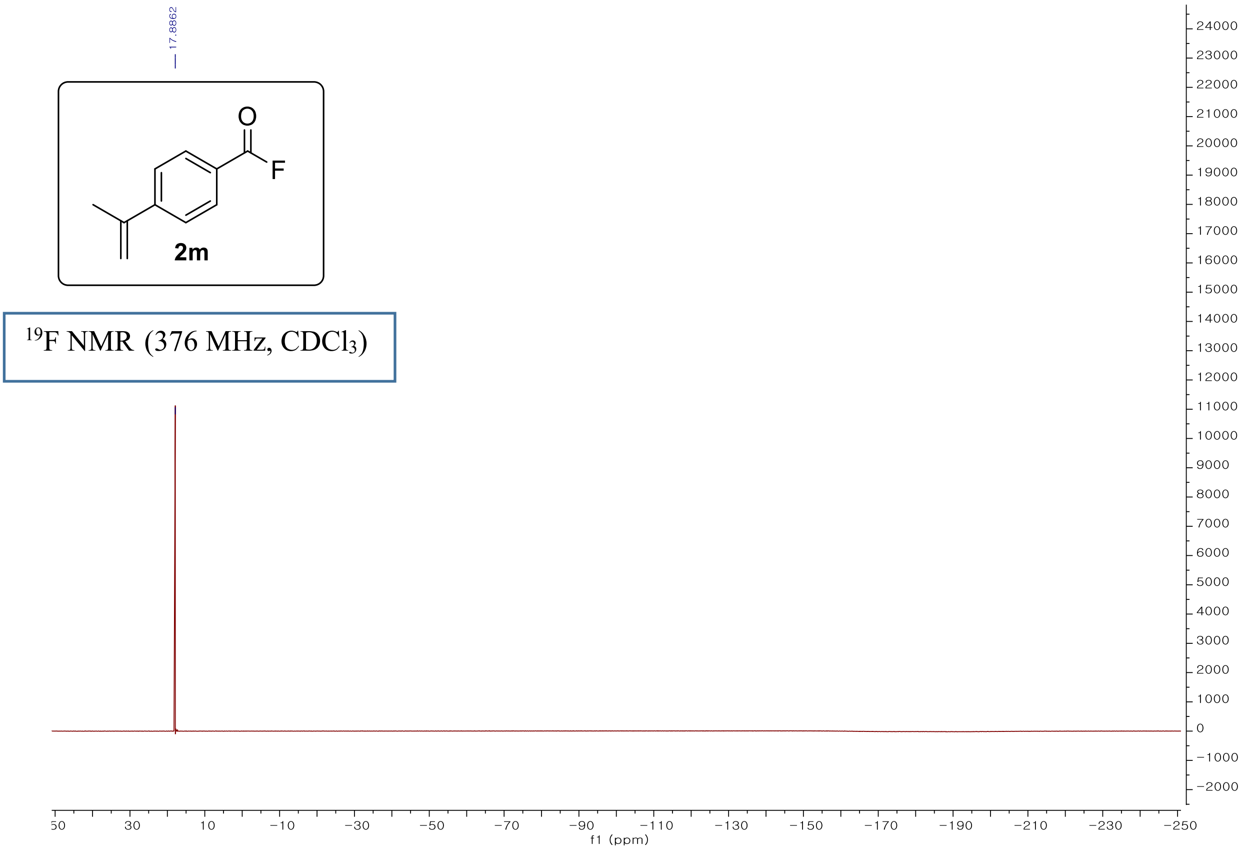
$^{1}$H NMR (500 MHz, CDCl$_3$)



20.0721
O
F
O
O
2l
$^{19}$F NMR (376 MHz, CDCl$_3$)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
−260
f1 (ppm)

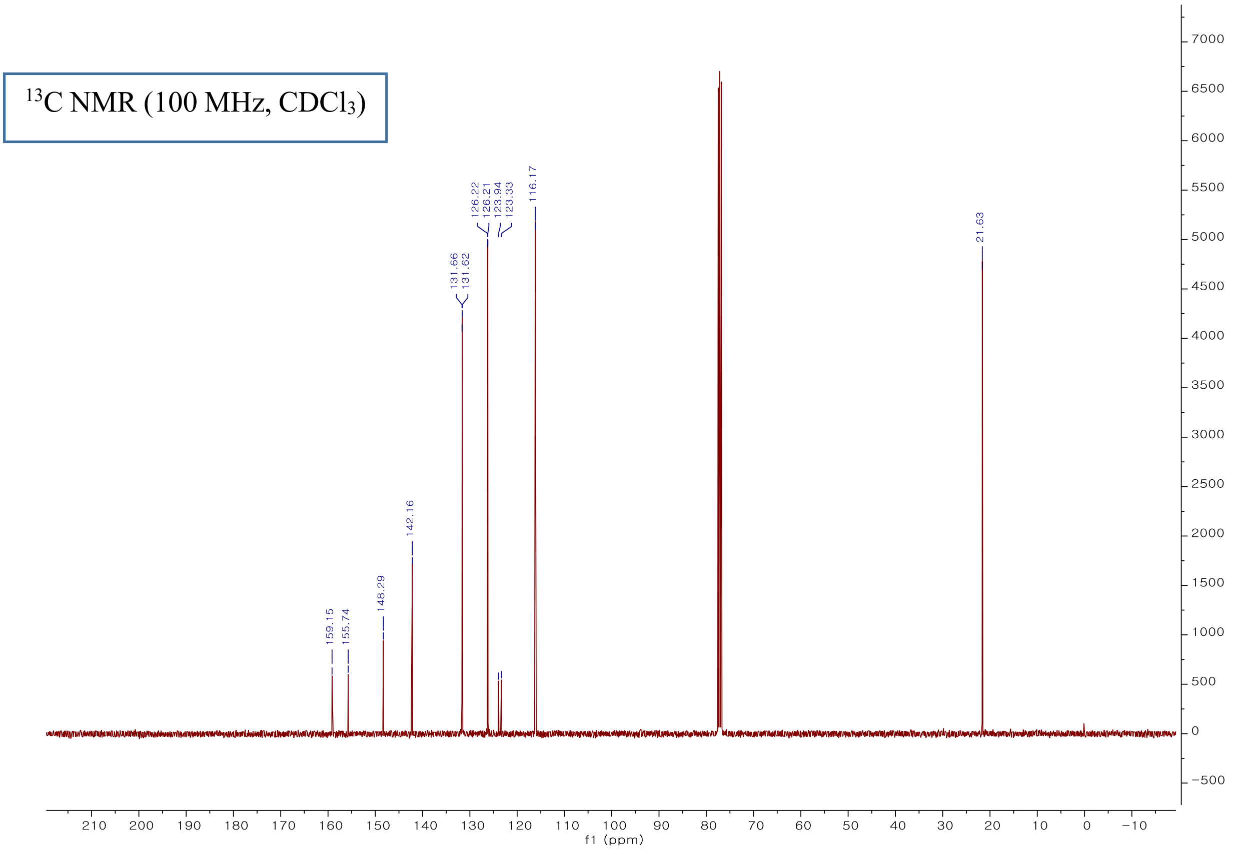


8.0064
8.0026
7.9933
7.9895
7.6009
7.5981
7.5944
7.5875
7.5838
7.5810
5.5279
5.5258
5.5239
5.2793
5.2764
5.2736
2.1865
2.1840
2.1819
O
F
2m
$^1$H NMR (500 MHz, CDCl$_3$)
1.96
2.00
1.00
1.01
3.09
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

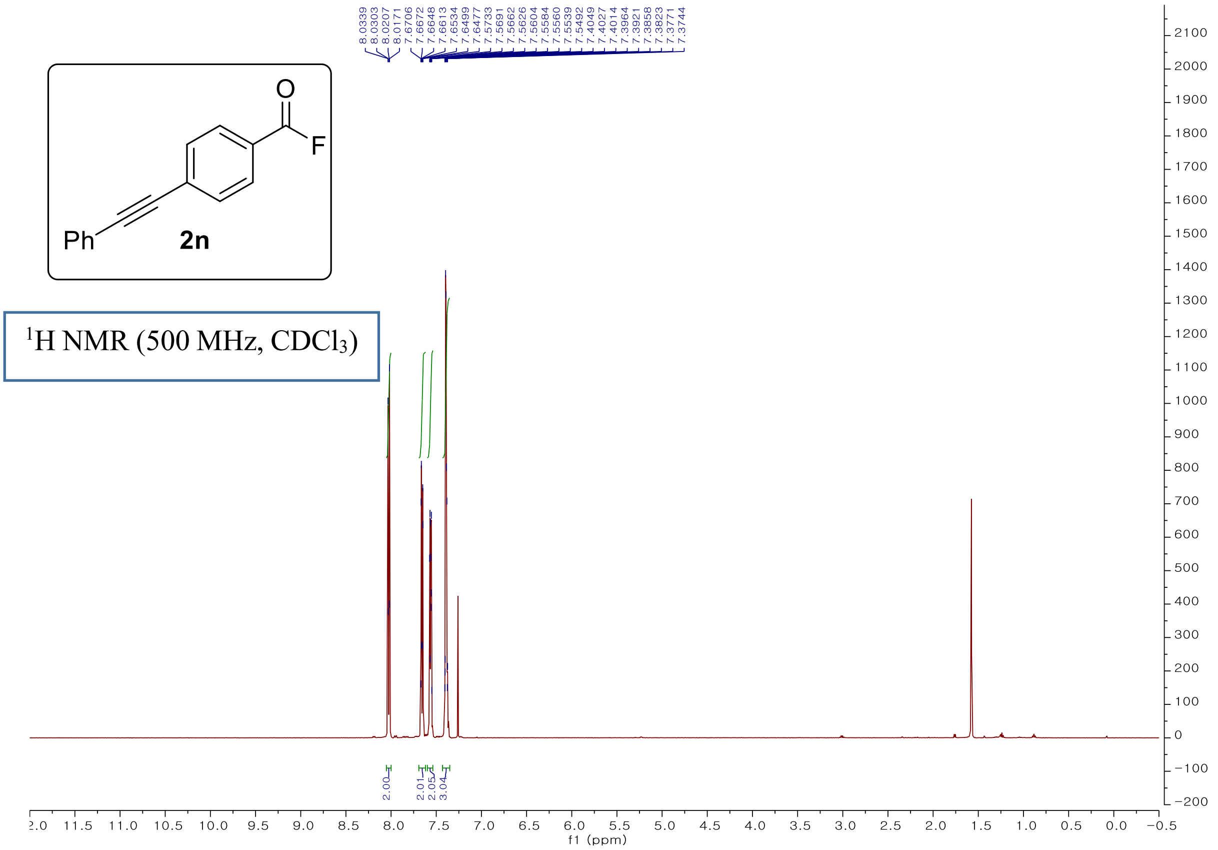


**2m**

$^{19}$F NMR (376 MHz, CDCl$_3$)

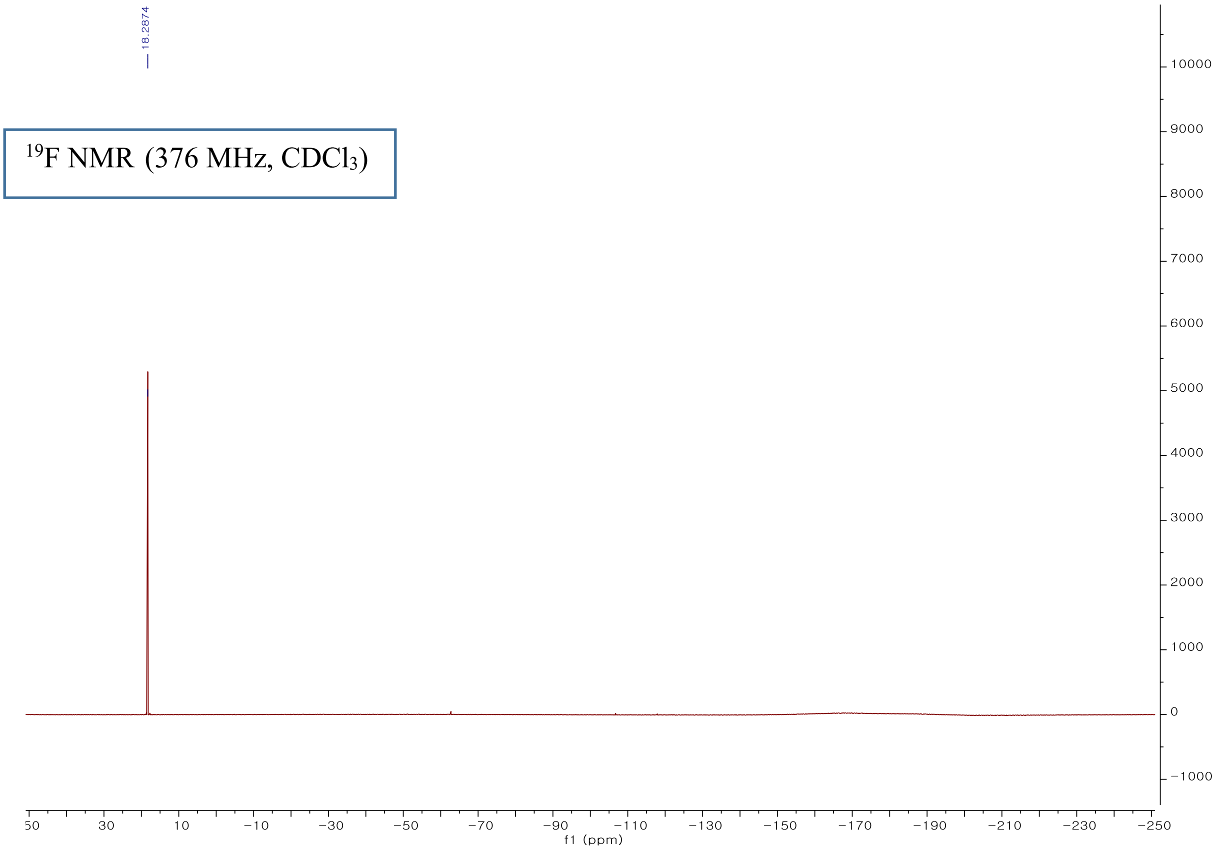


$^{13}$C NMR (100 MHz, CDCl$_3$)

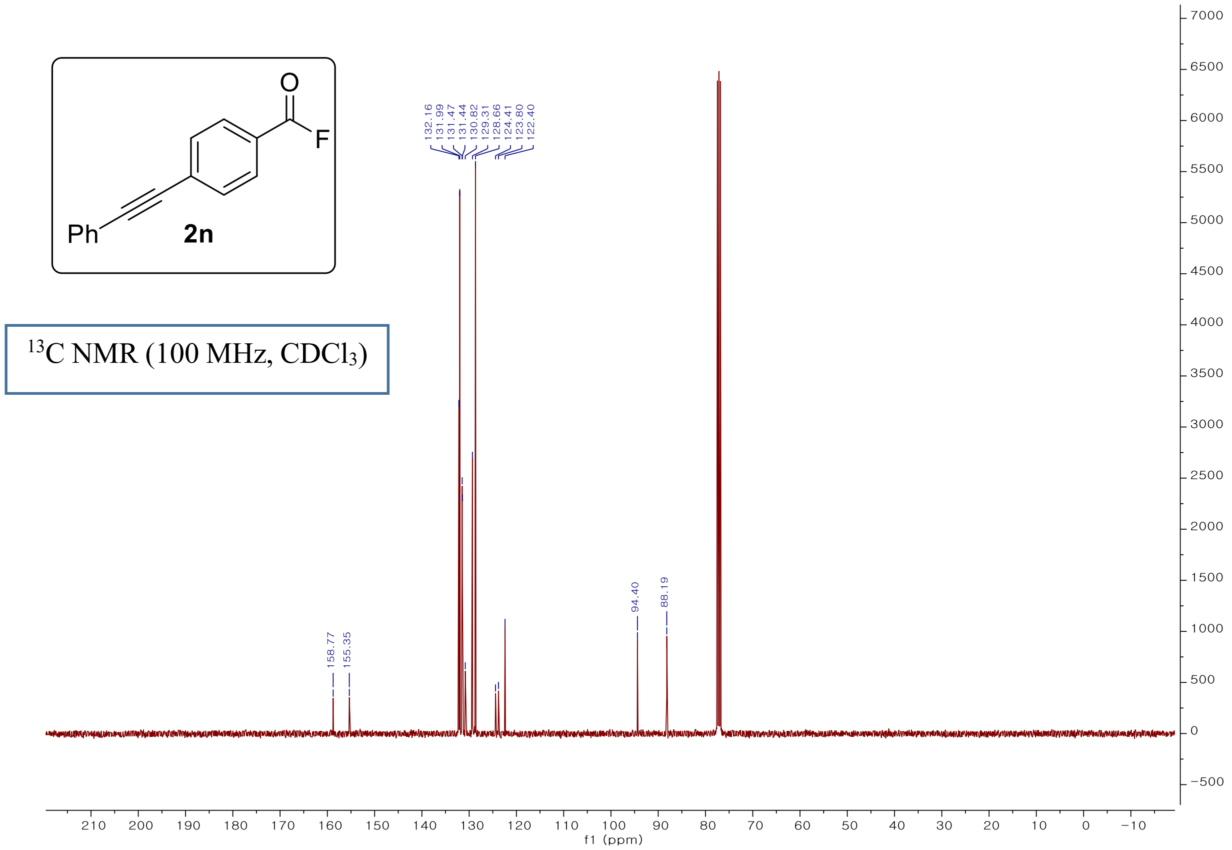


**2n**

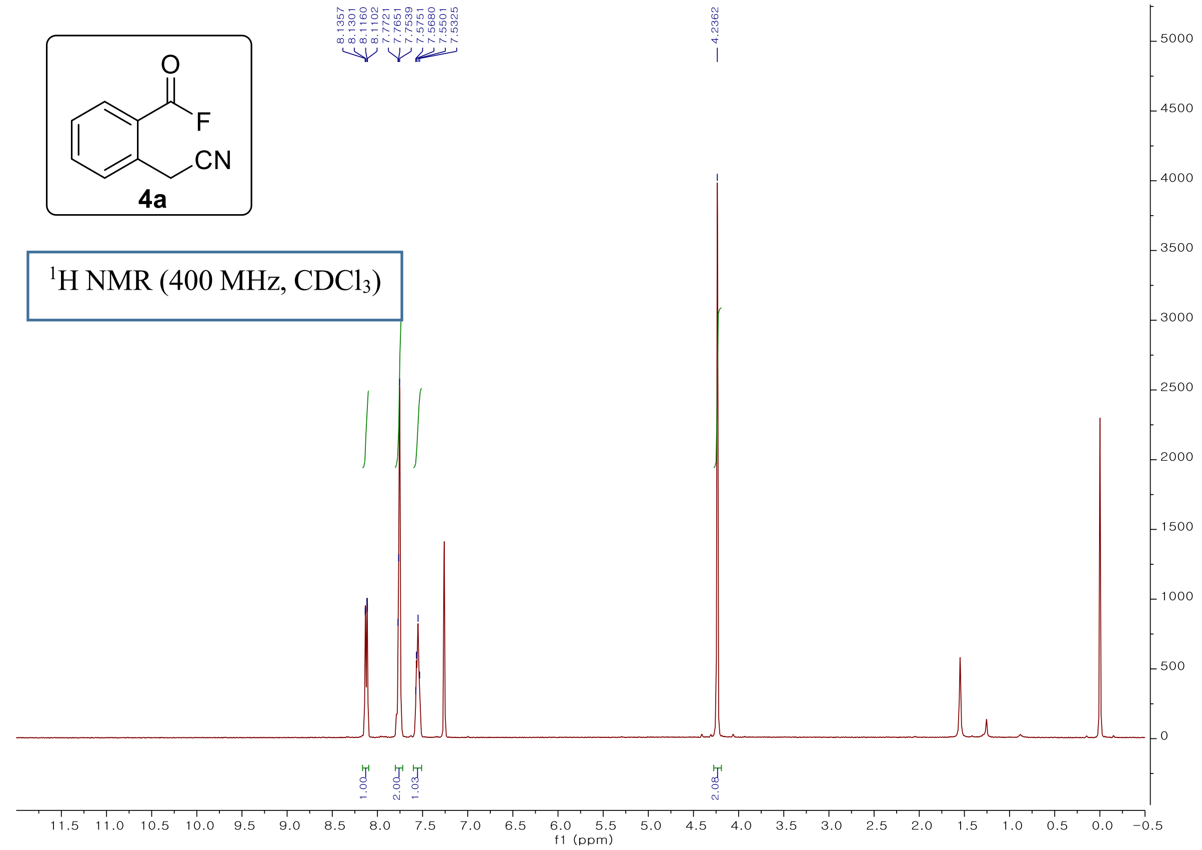
$^{1}$H NMR (500 MHz, CDCl$_3$)



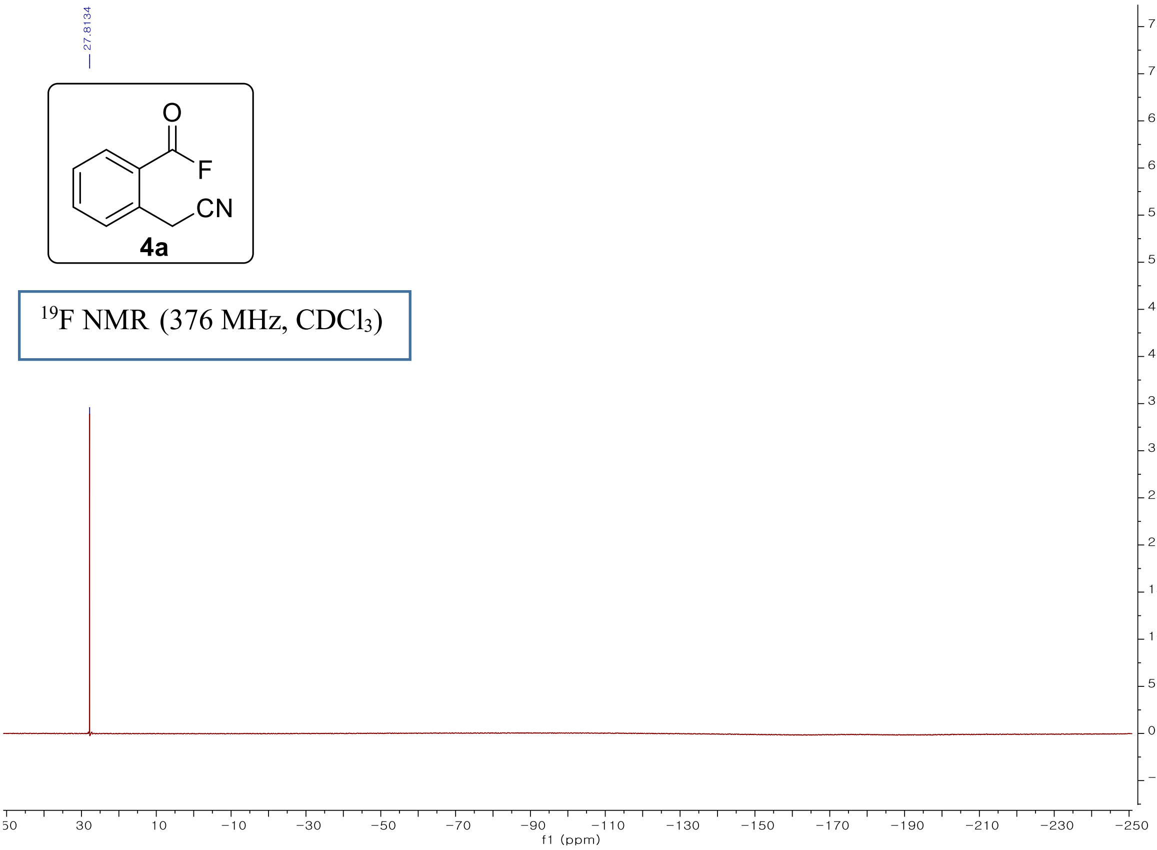
$^{19}$F NMR (376 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)

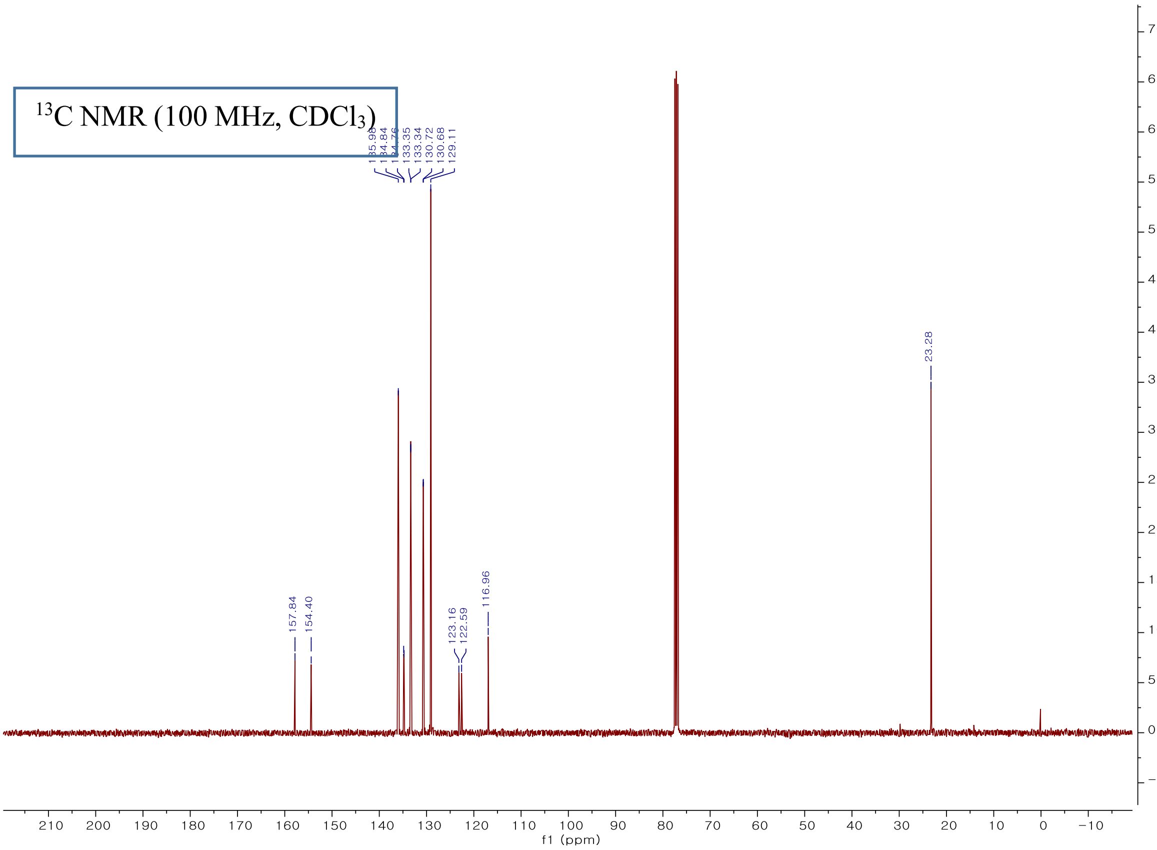


$^1$H NMR (400 MHz, CDCl$_3$)

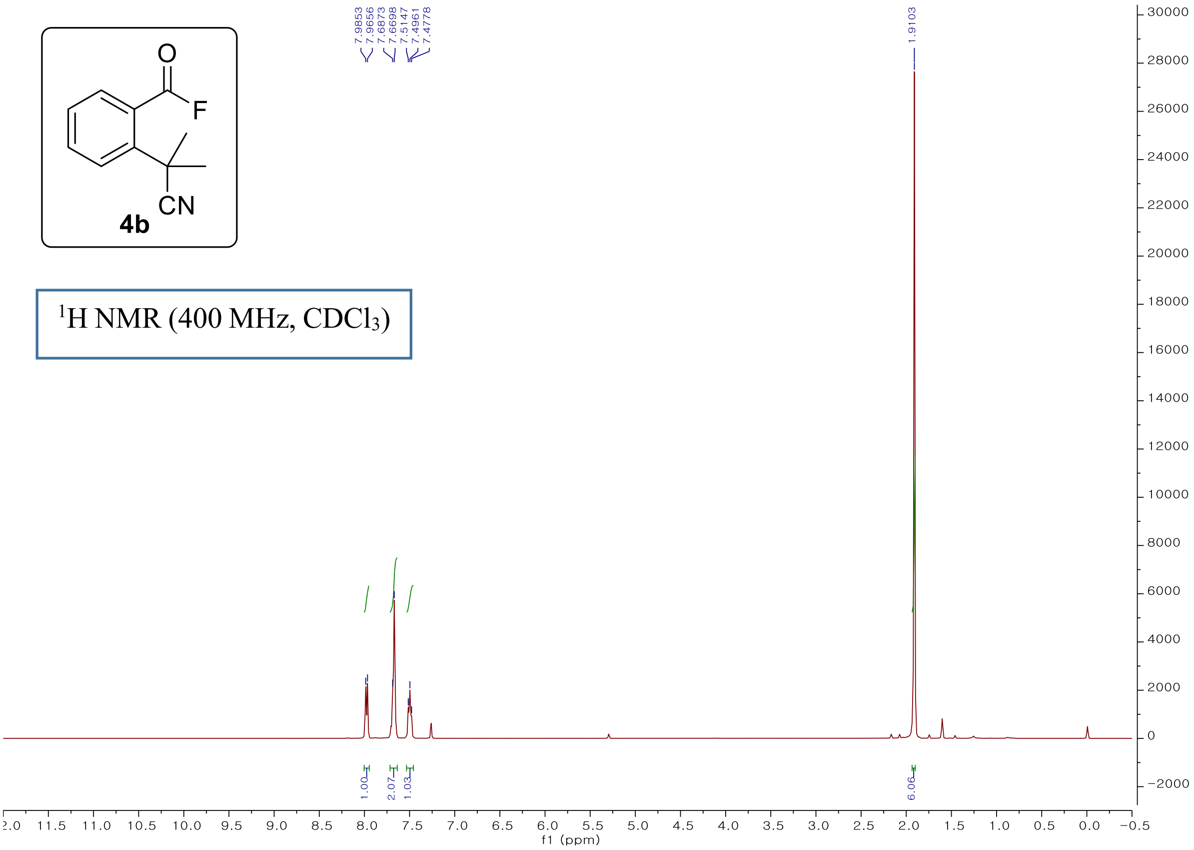


**4a**

$^{19}$F NMR (376 MHz, CDCl$_3$)

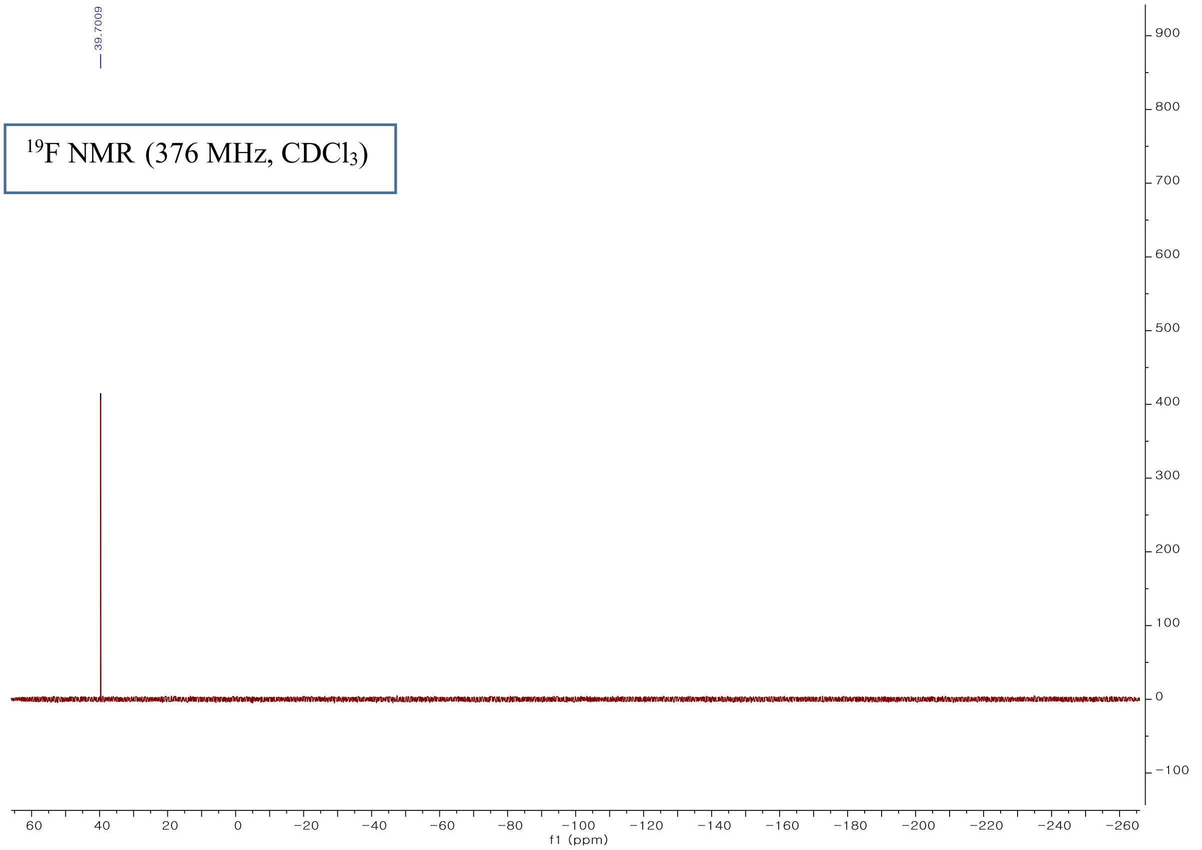


$^{13}$C NMR (100 MHz, CDCl$_3$)

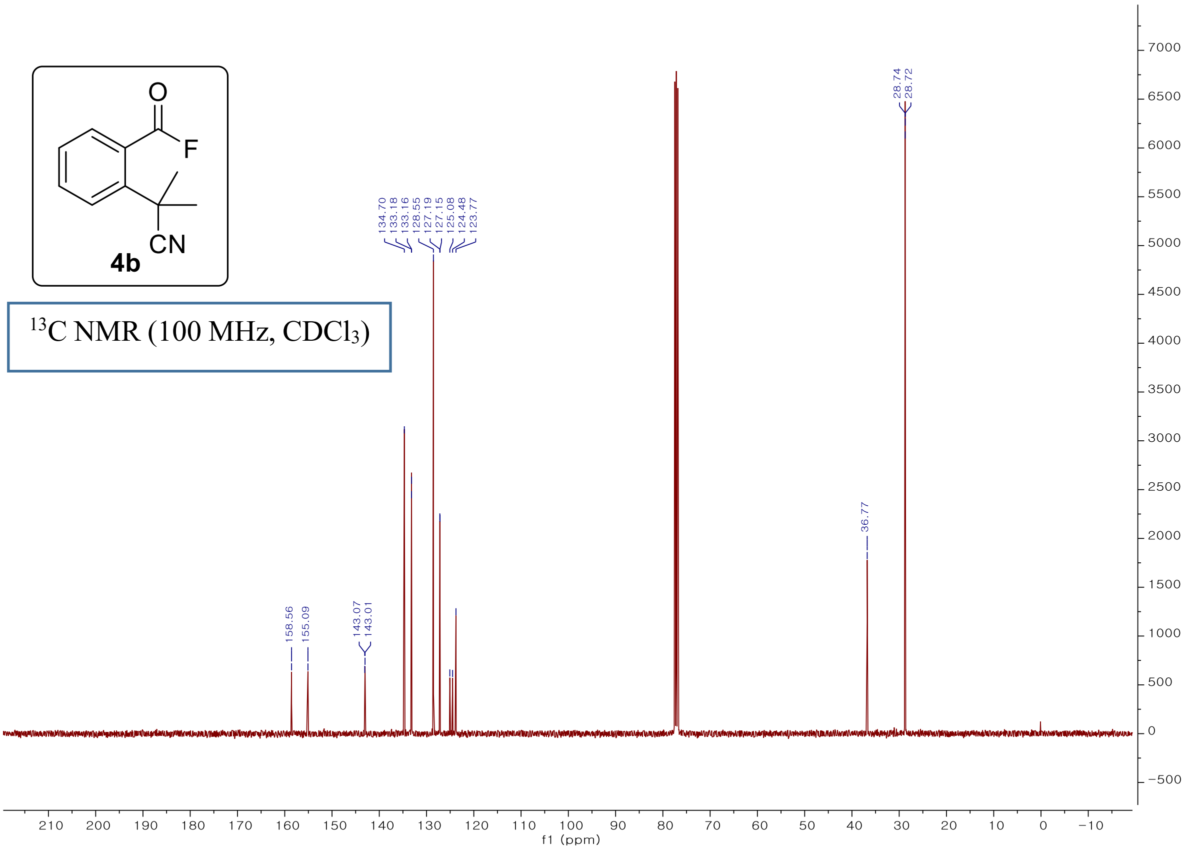


**4b**

$^1$H NMR (400 MHz, $CDCl_3$)

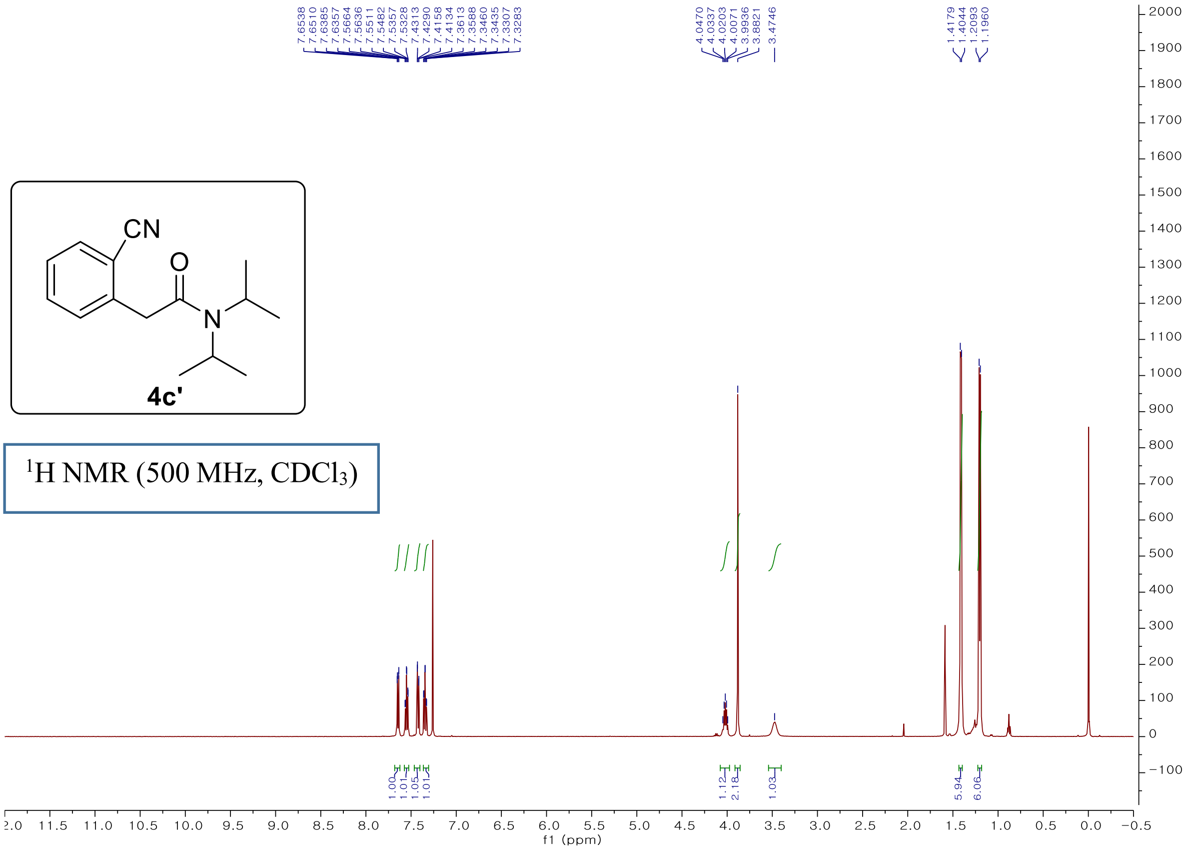


$^{19}$F NMR (376 MHz, $CDCl_3$)



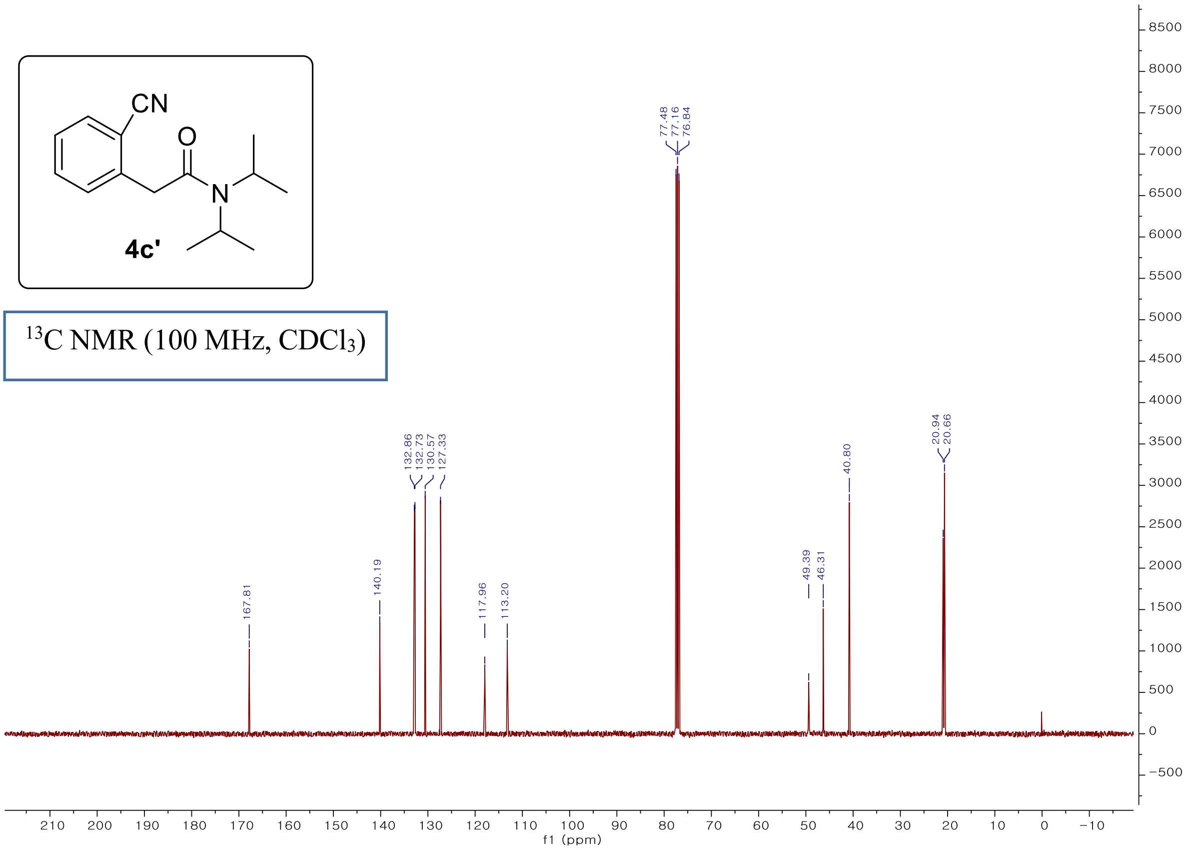
**4b**

$^{13}$C NMR (100 MHz, CDCl$_3$)



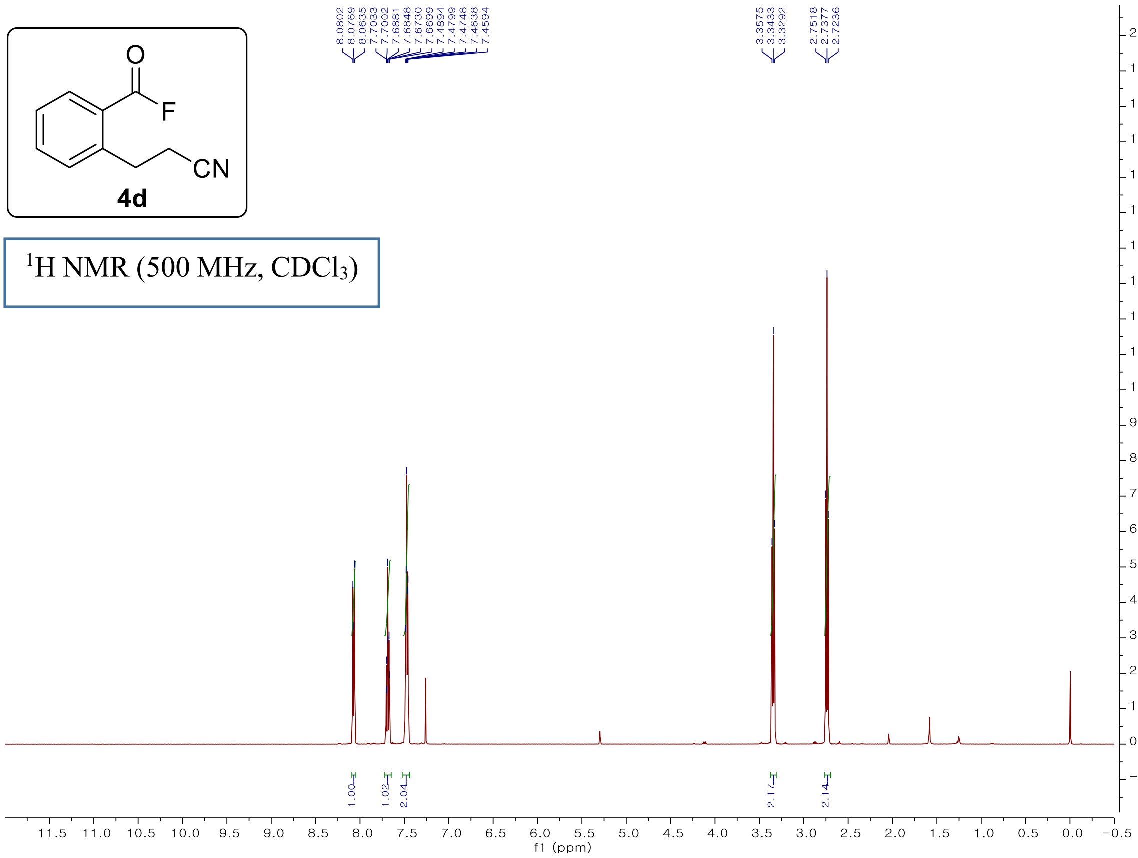
**4c'**

$^{1}$H NMR (500 MHz, CDCl$_3$)



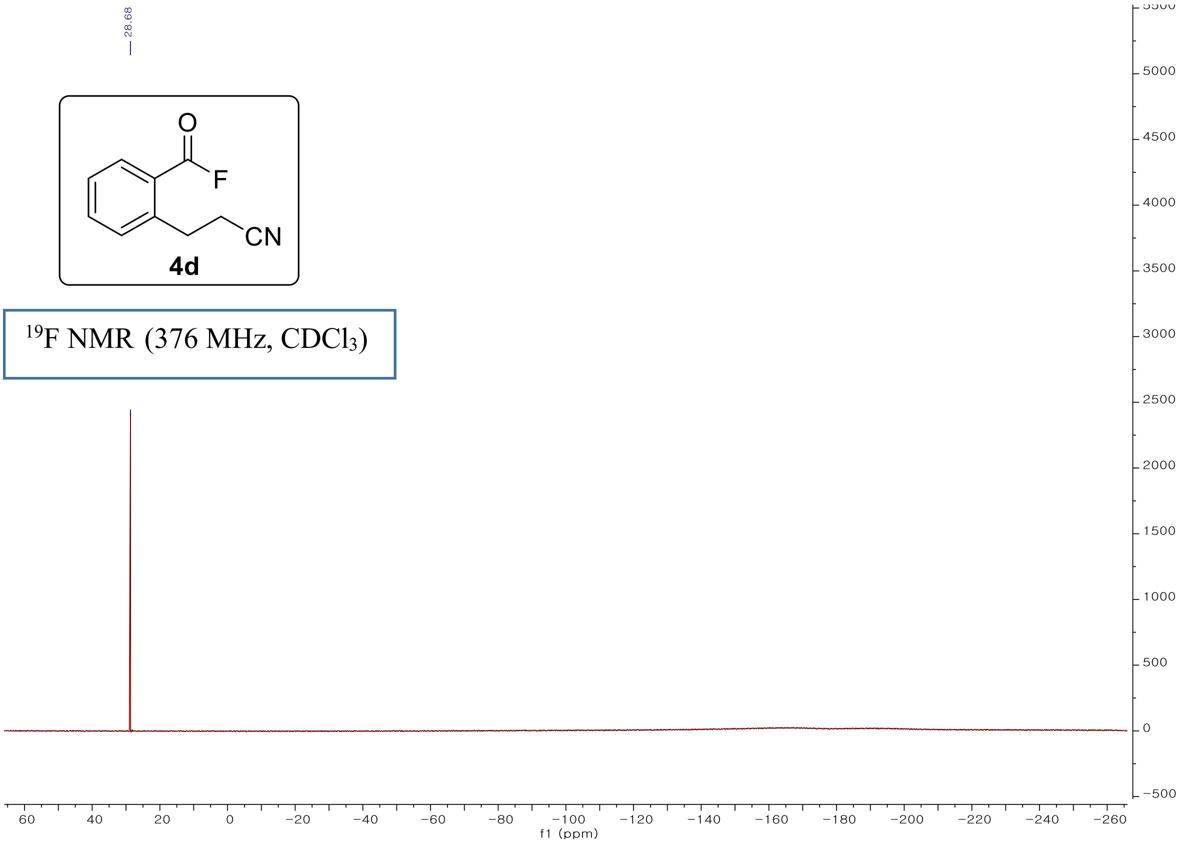
**4c'**

$^{13}$C NMR (100 MHz, CDCl$_3$)



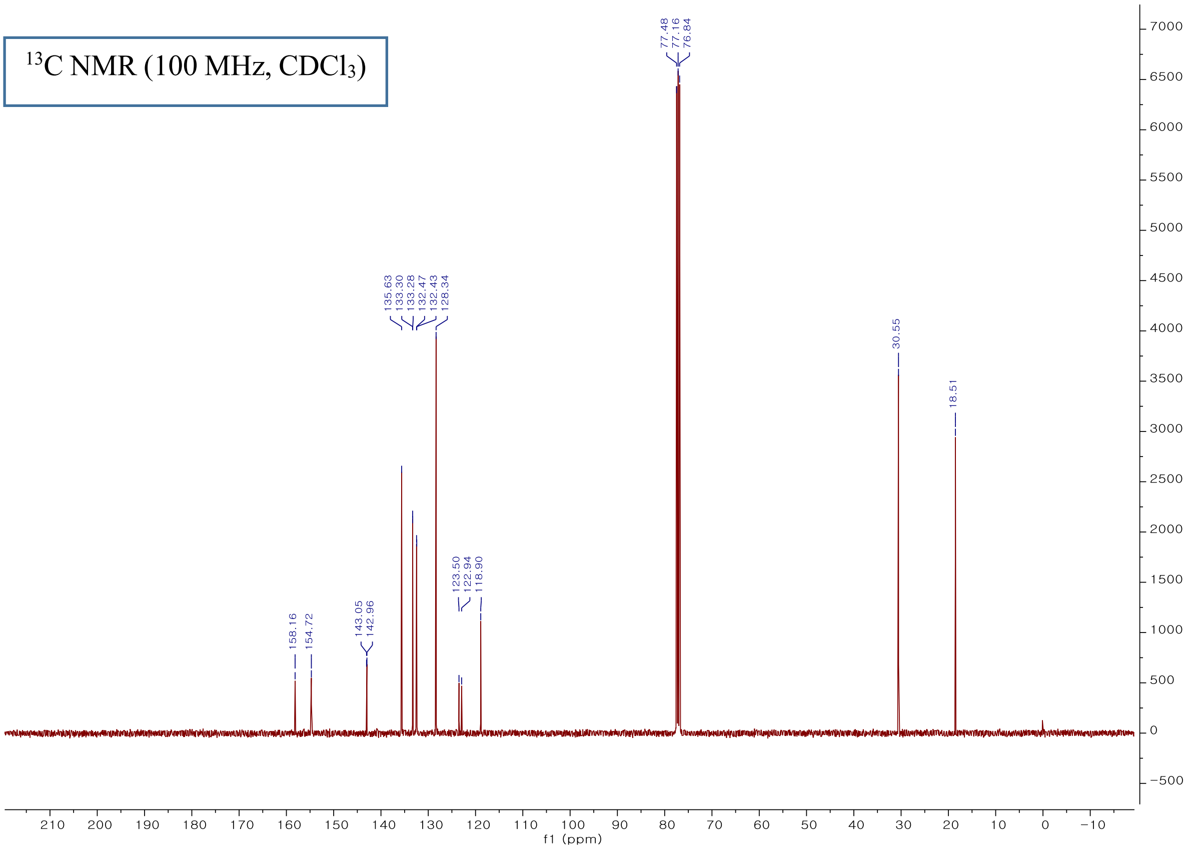
**4d**

$^{1}$H NMR (500 MHz, CDCl$_3$)

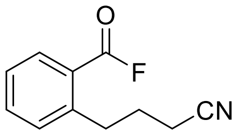


**4d**

$^{19}$F NMR (376 MHz, $CDCl_3$)

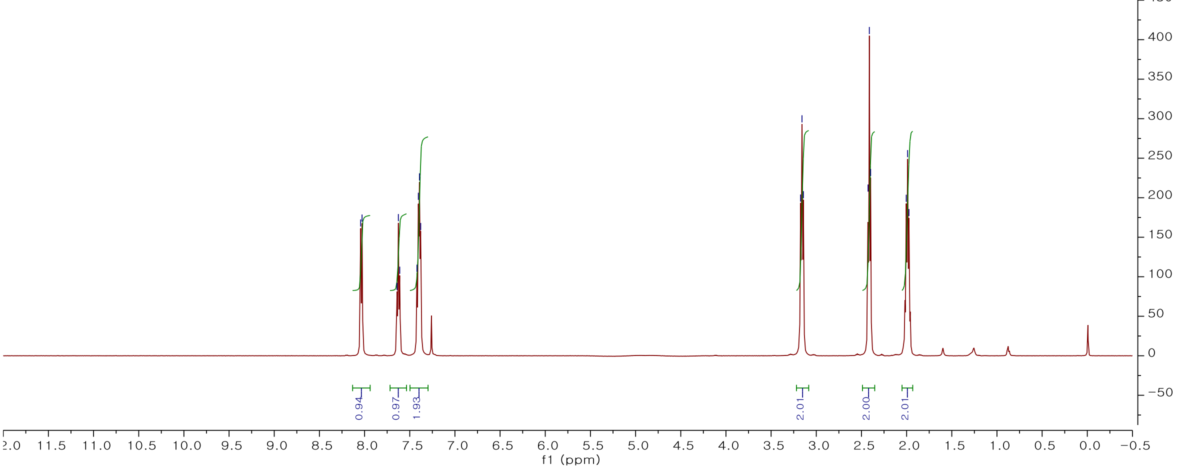


$^{13}$C NMR (100 MHz, $CDCl_3$)

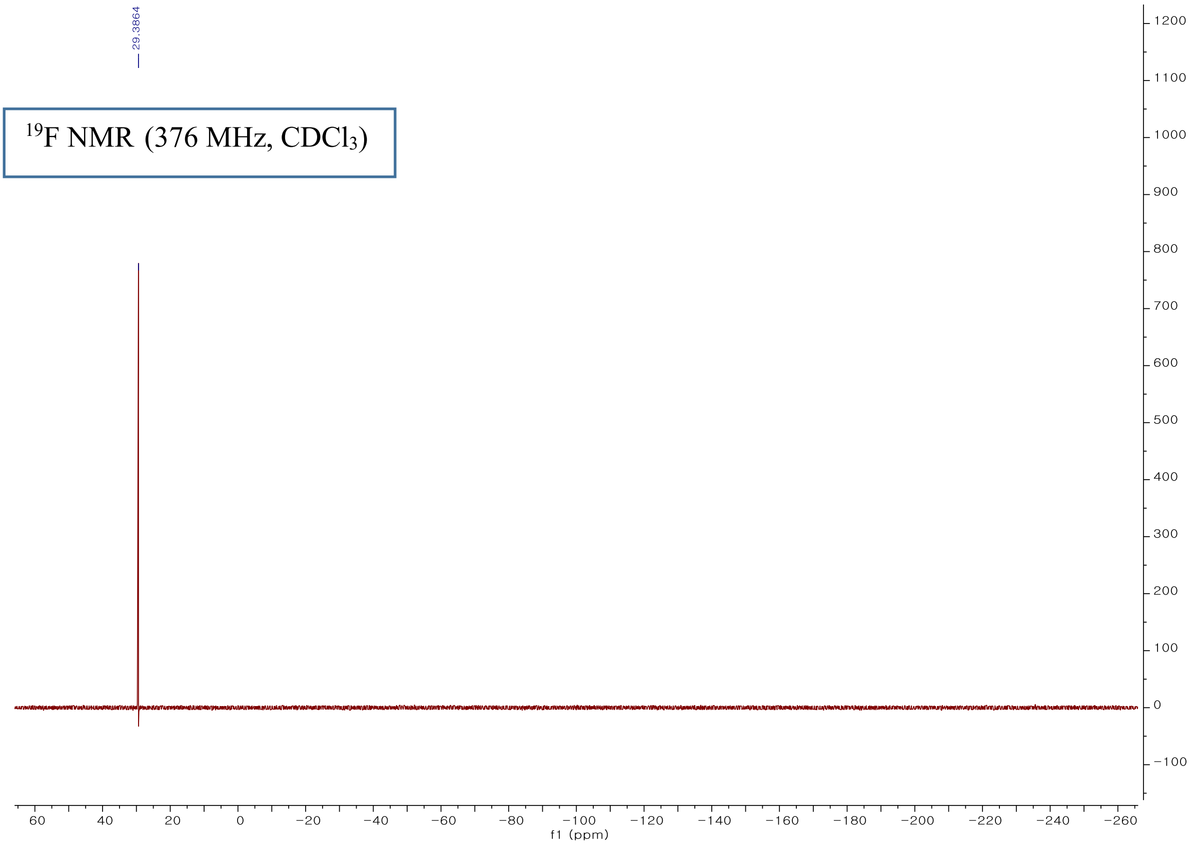


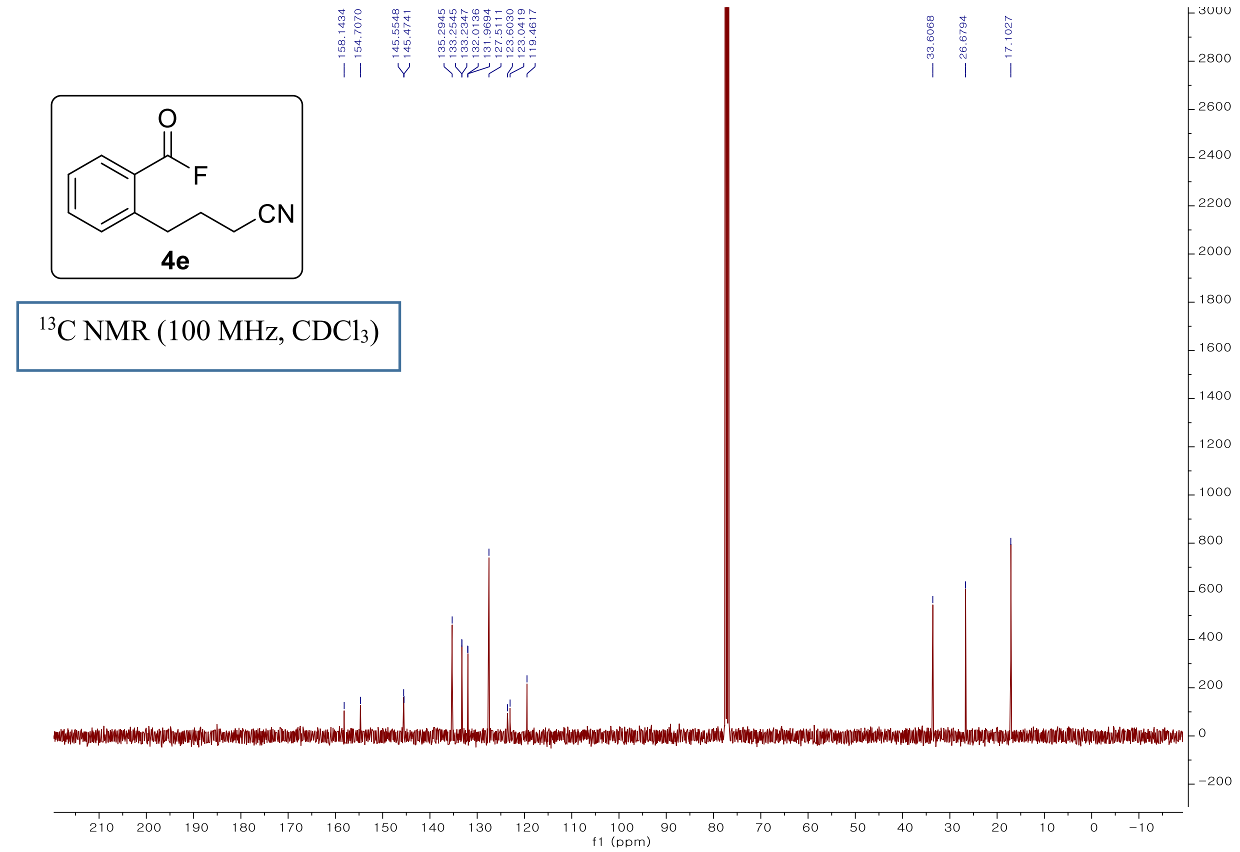
**4e**

$^1$H NMR (500 MHz, CDCl$_3$)



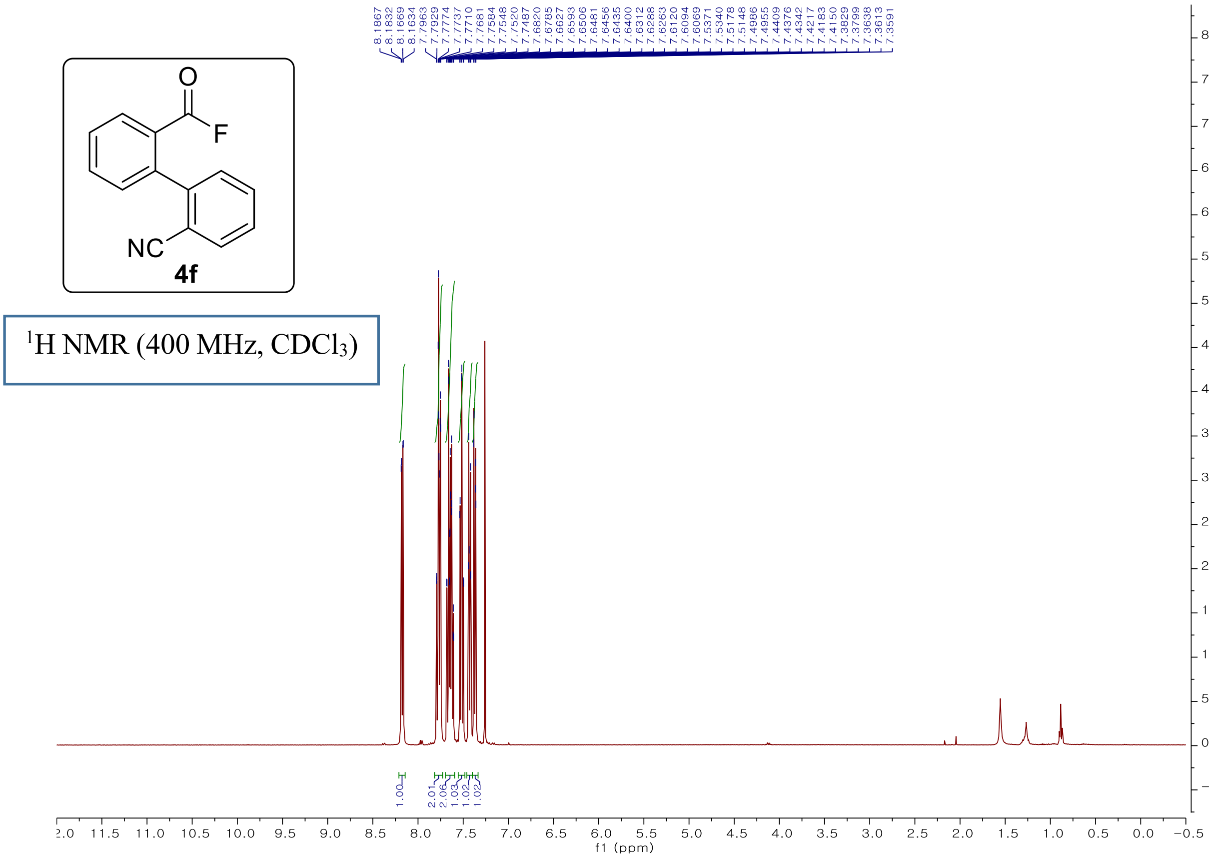
$^{19}$F NMR (376 MHz, CDCl$_3$)





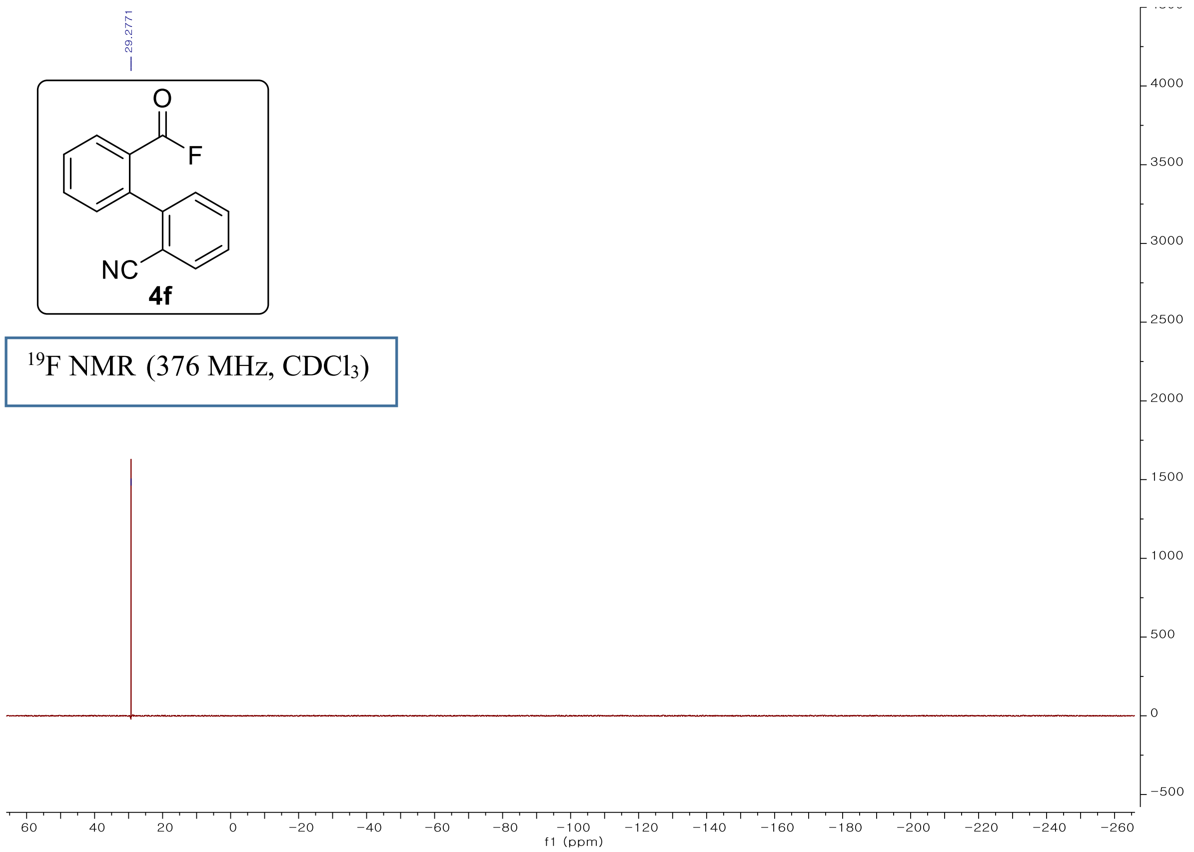
**4e**

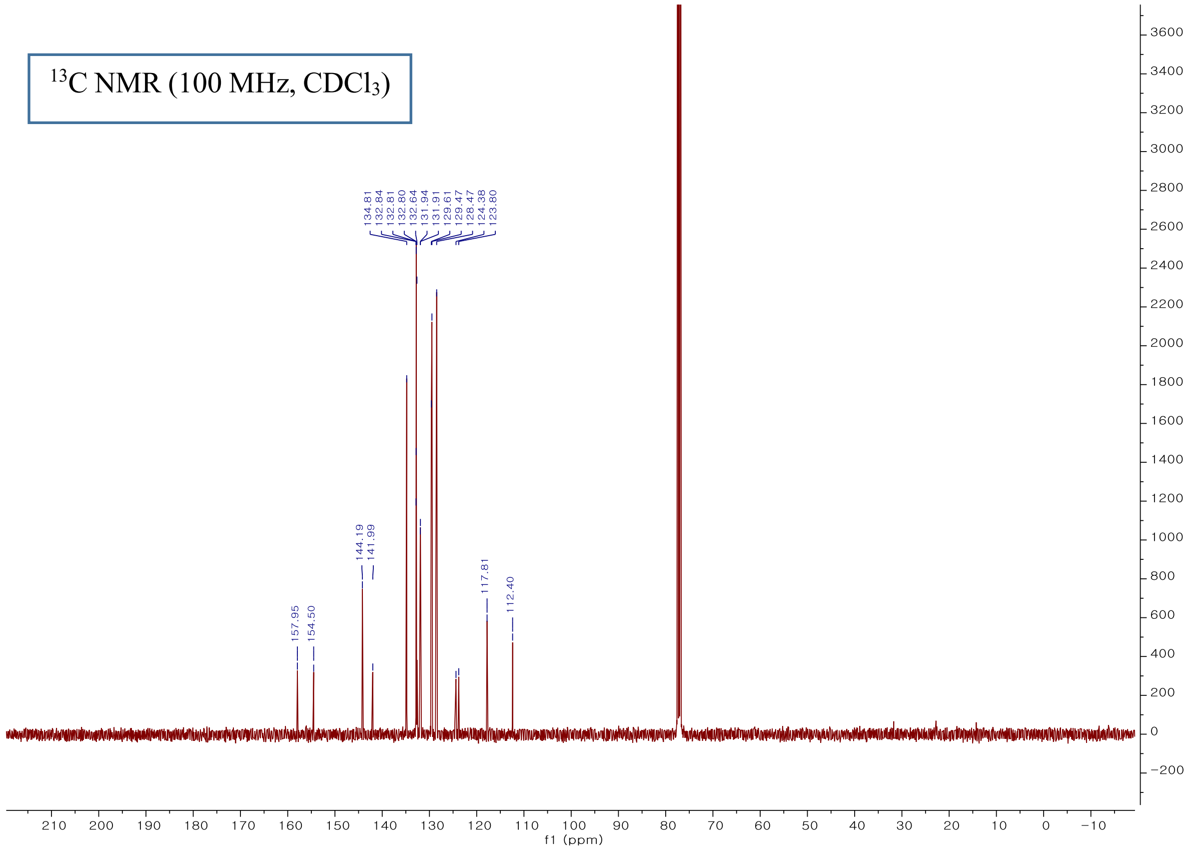
$^{13}$C NMR (100 MHz, CDCl$_3$)

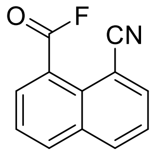


**4f**

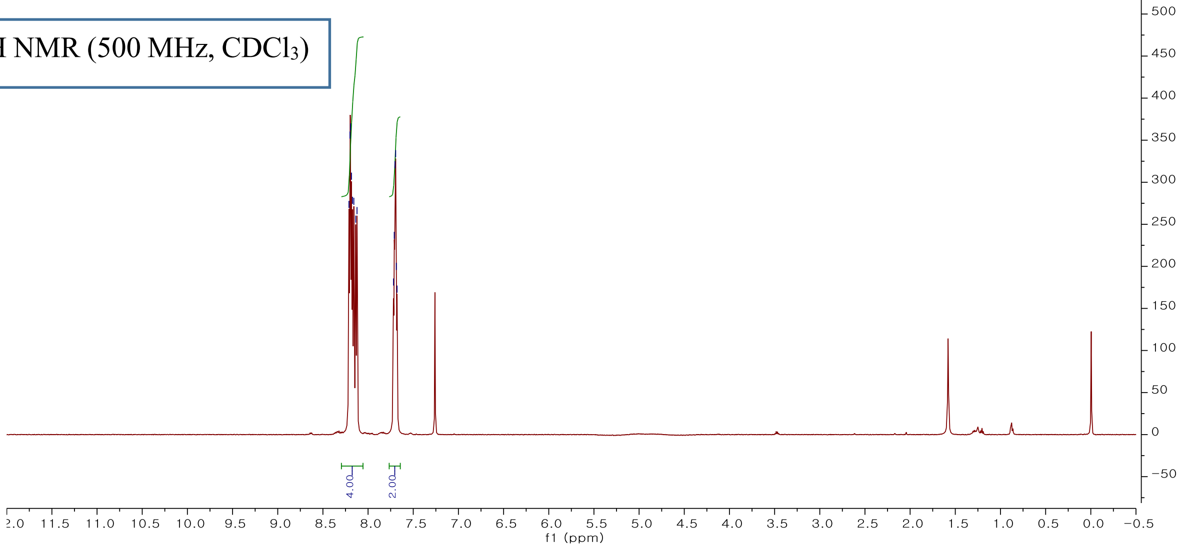
$^{1}$H NMR (400 MHz, CDCl$_3$)


29.2771
O
F
NC
4f
19F NMR (376 MHz, CDCl3)
4000
3500
3000
2500
2000
1500
1000
500
0
−500
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
−260
f1 (ppm)

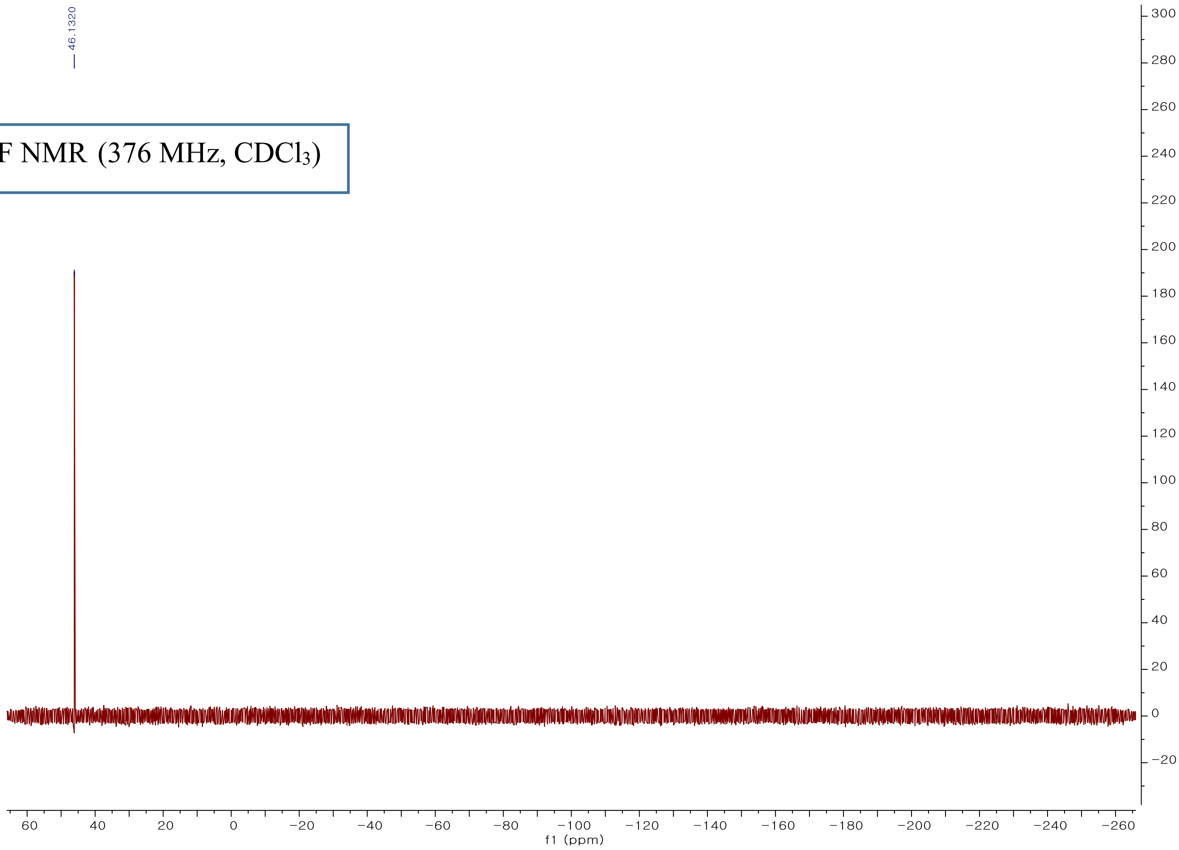

13C NMR (100 MHz, CDCl3)
157.95
154.50
144.19
141.99
134.81
132.84
132.81
132.80
132.64
131.94
131.91
129.61
129.47
128.47
124.38
123.80
117.81
112.40
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



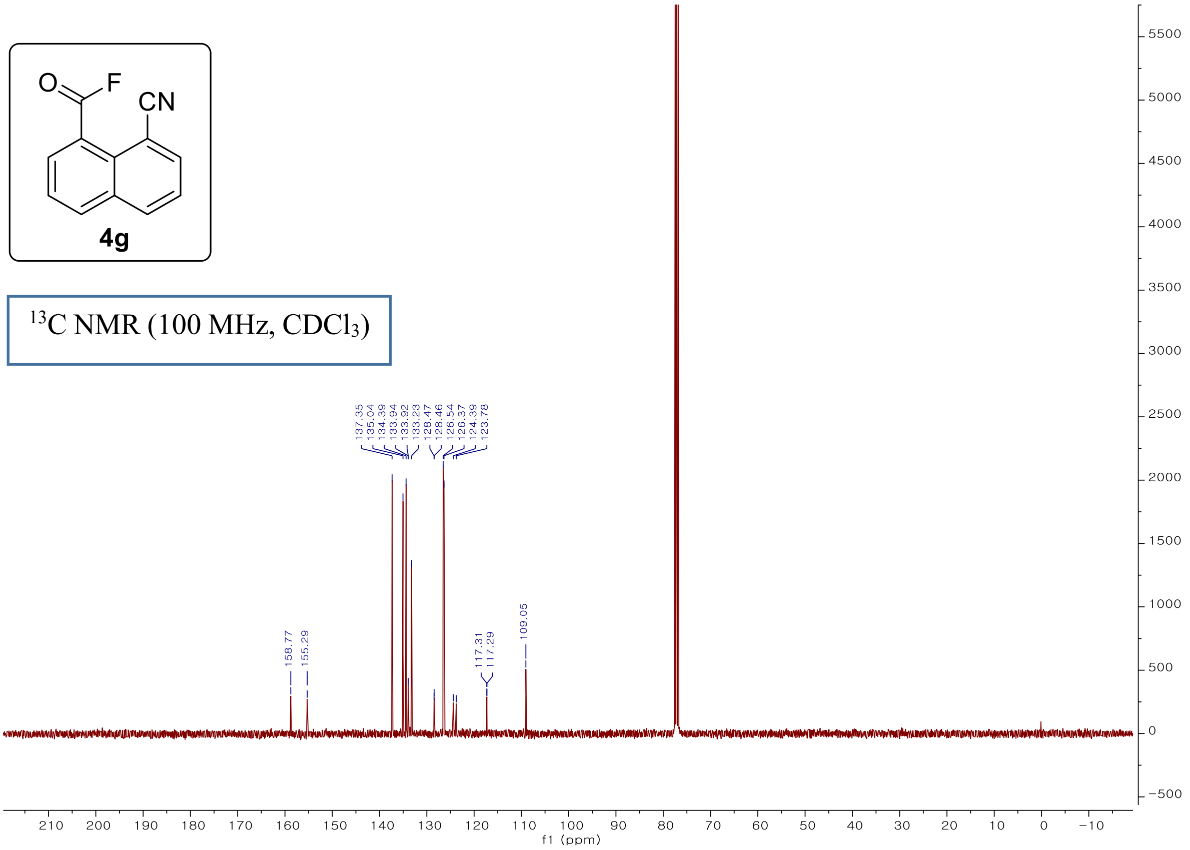
**4g**



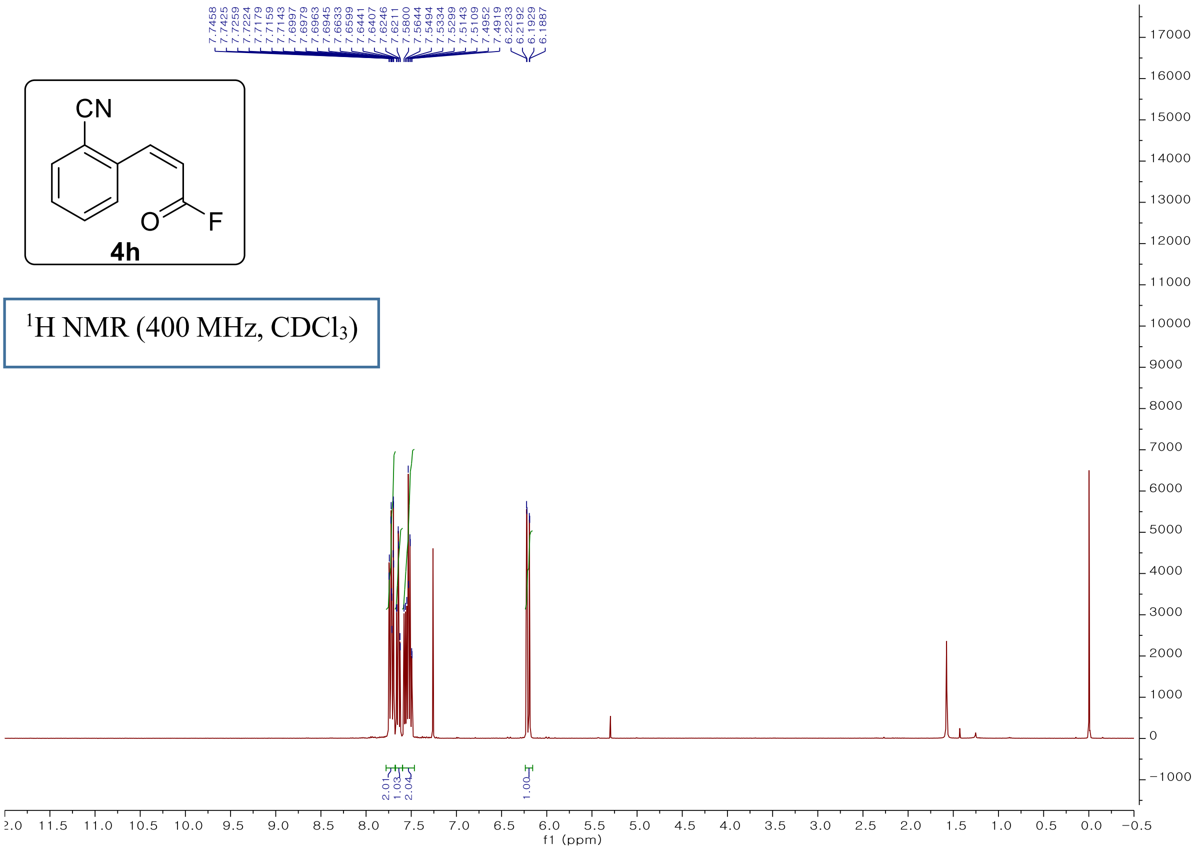
$^{1}$H NMR (500 MHz, CDCl$_3$)



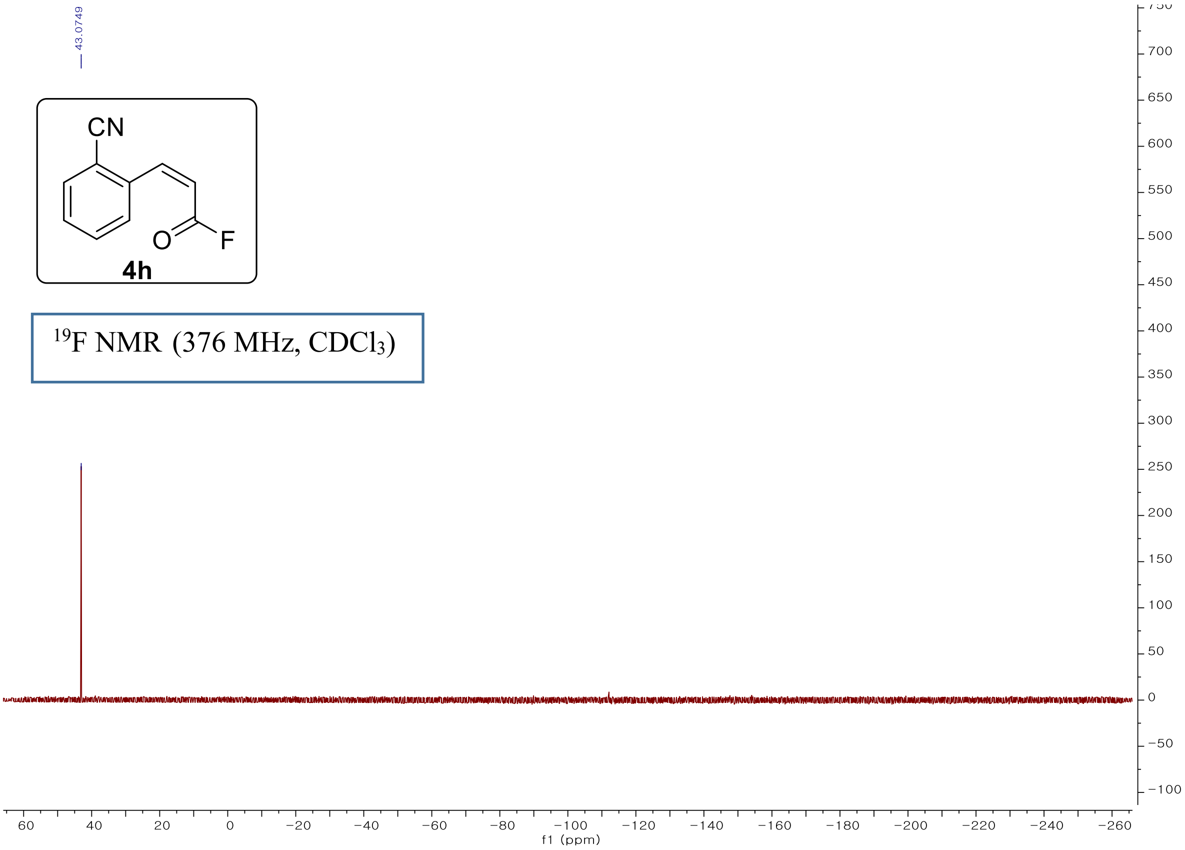
$^{19}$F NMR (376 MHz, CDCl$_3$)


**4g**

$^{13}$C NMR (100 MHz, $CDCl_3$)

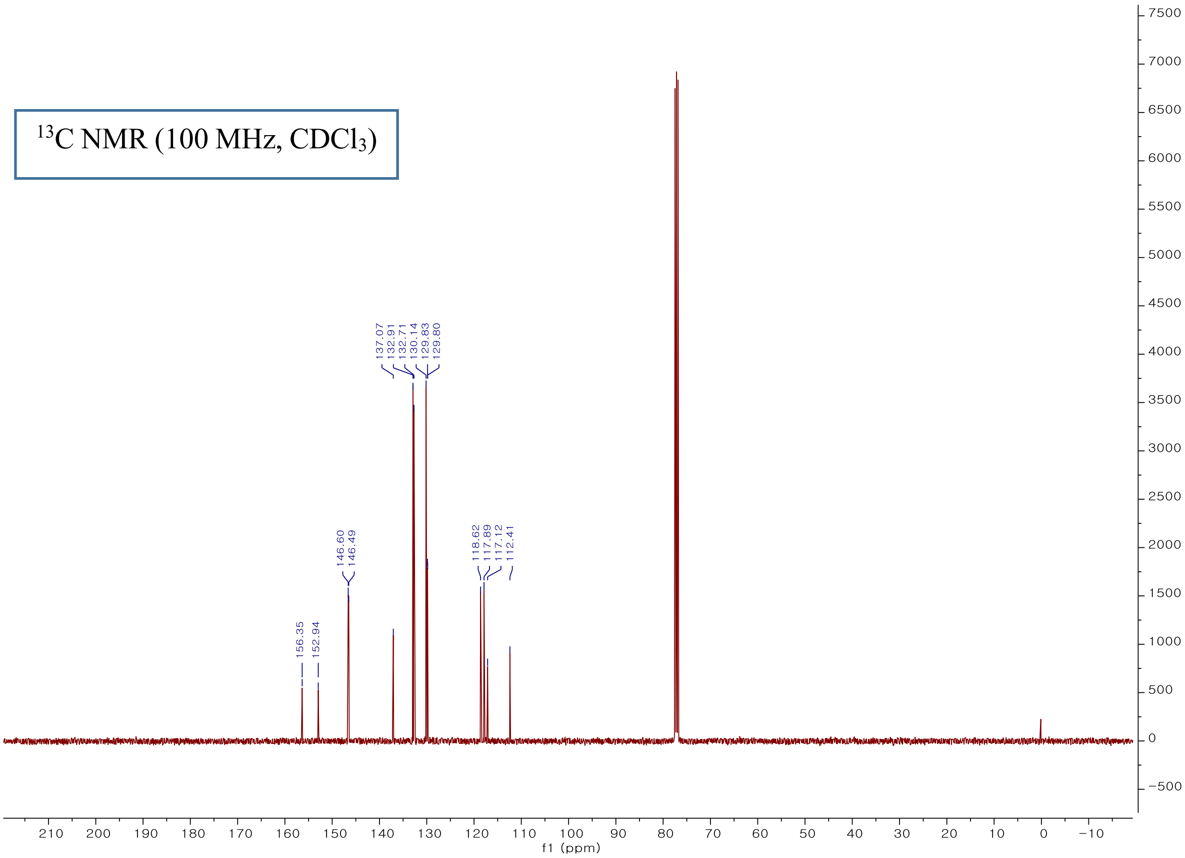

**4h**

$^1$H NMR (400 MHz, $CDCl_3$)

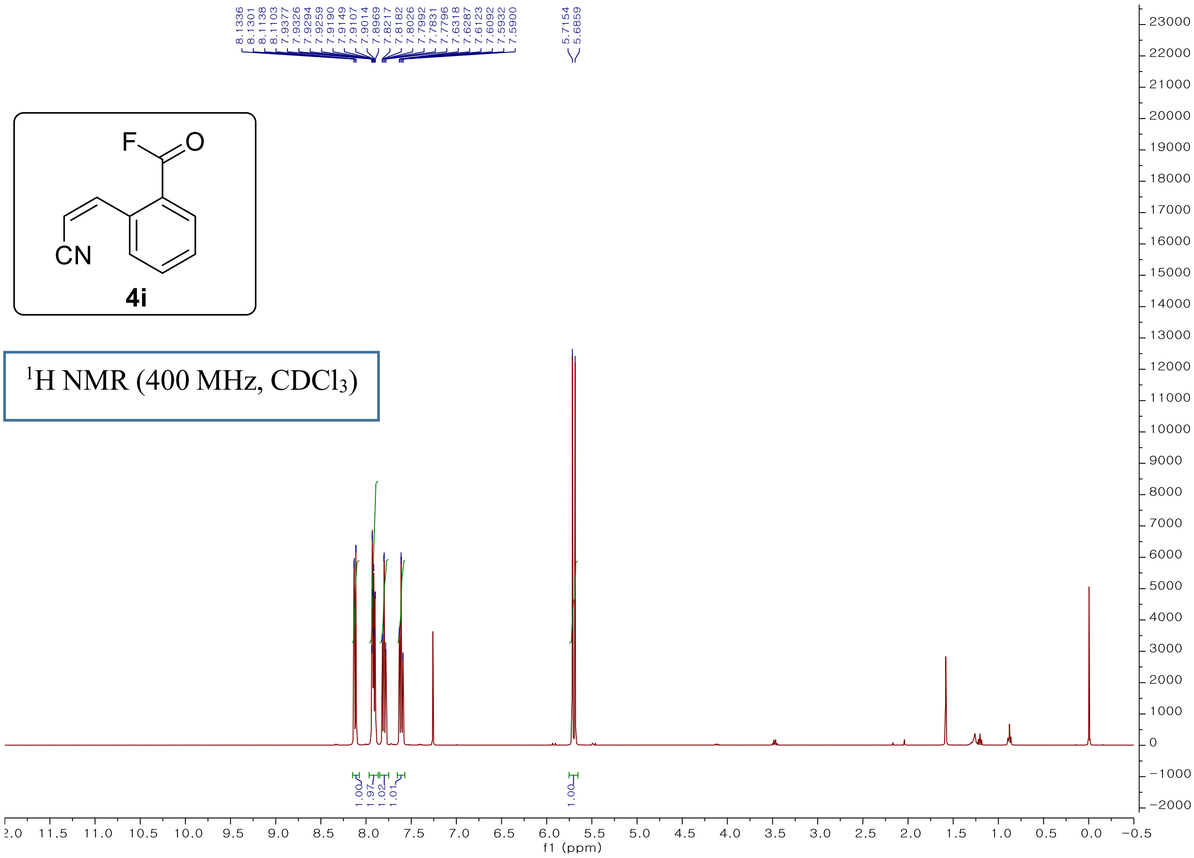


**4h**

$^{19}$F NMR (376 MHz, CDCl$_3$)

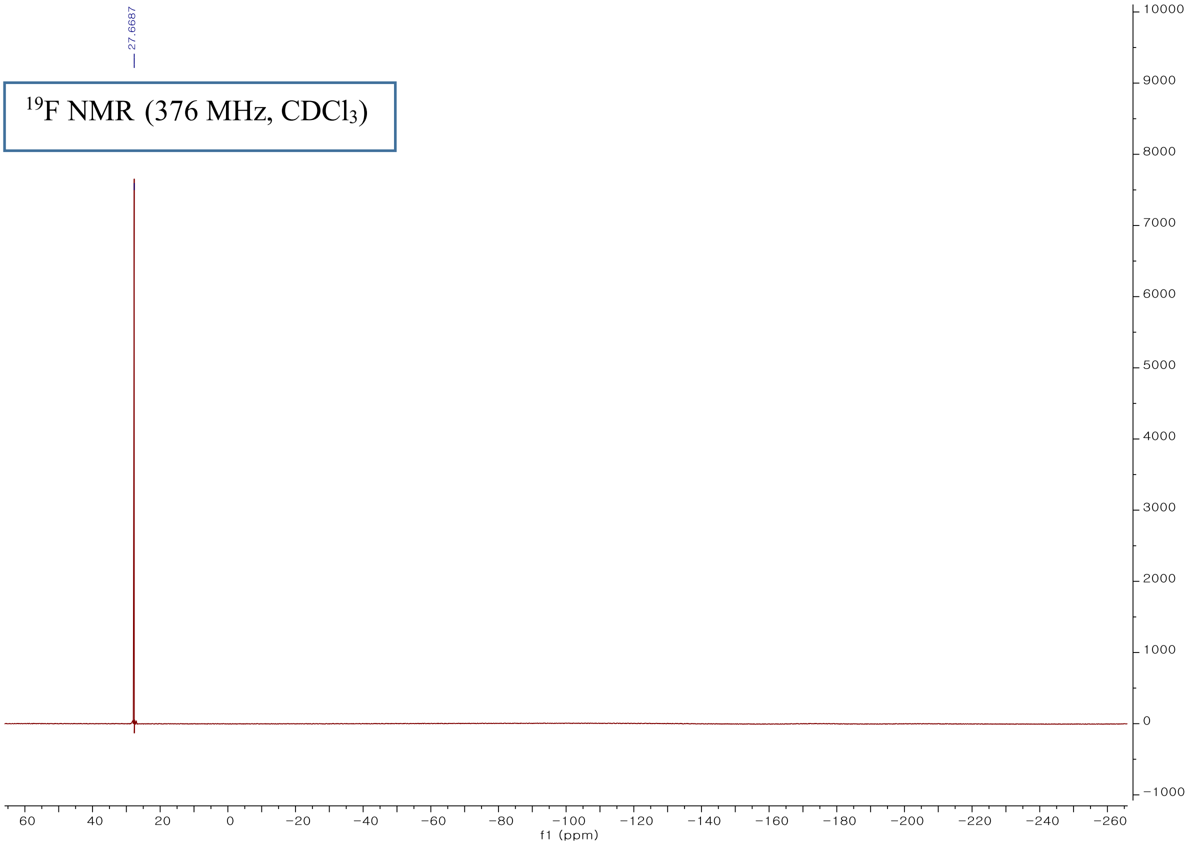


$^{13}$C NMR (100 MHz, CDCl$_3$)

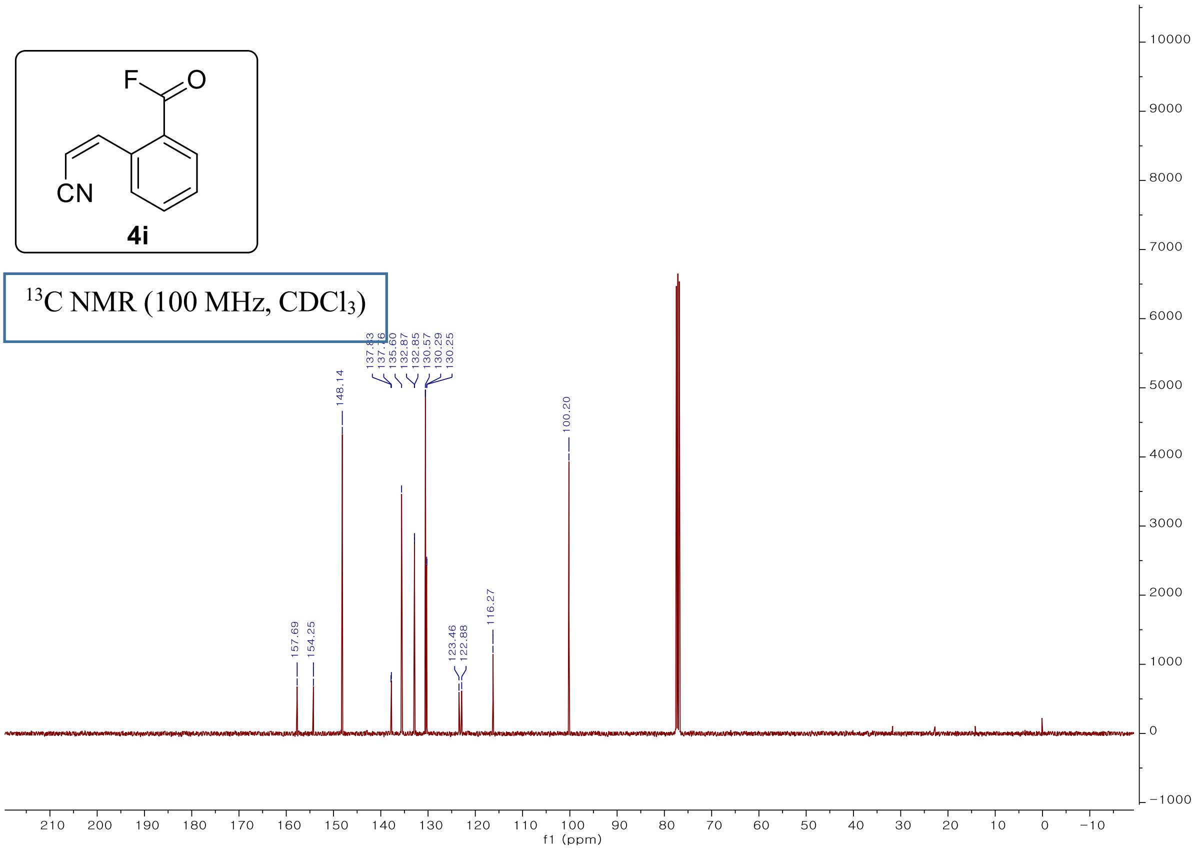


**4i**

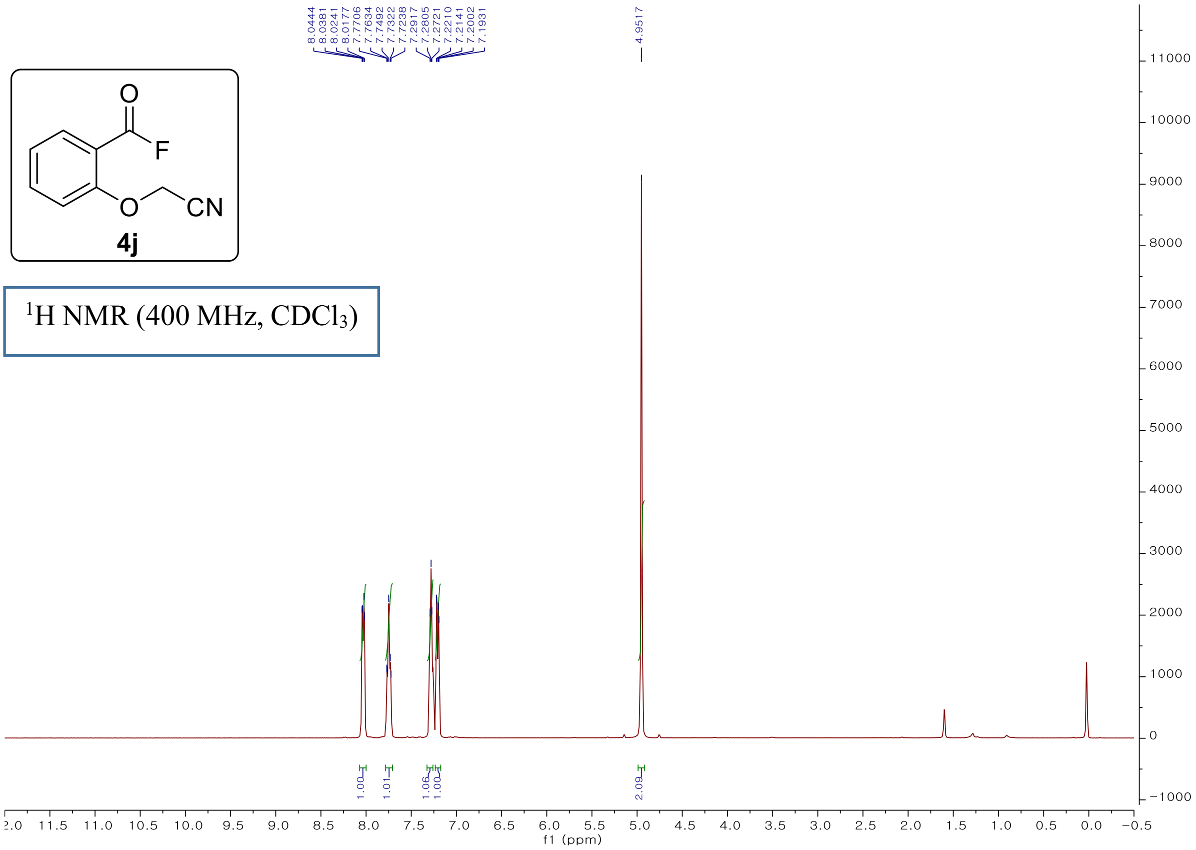
$^1$H NMR (400 MHz, CDCl$_3$)



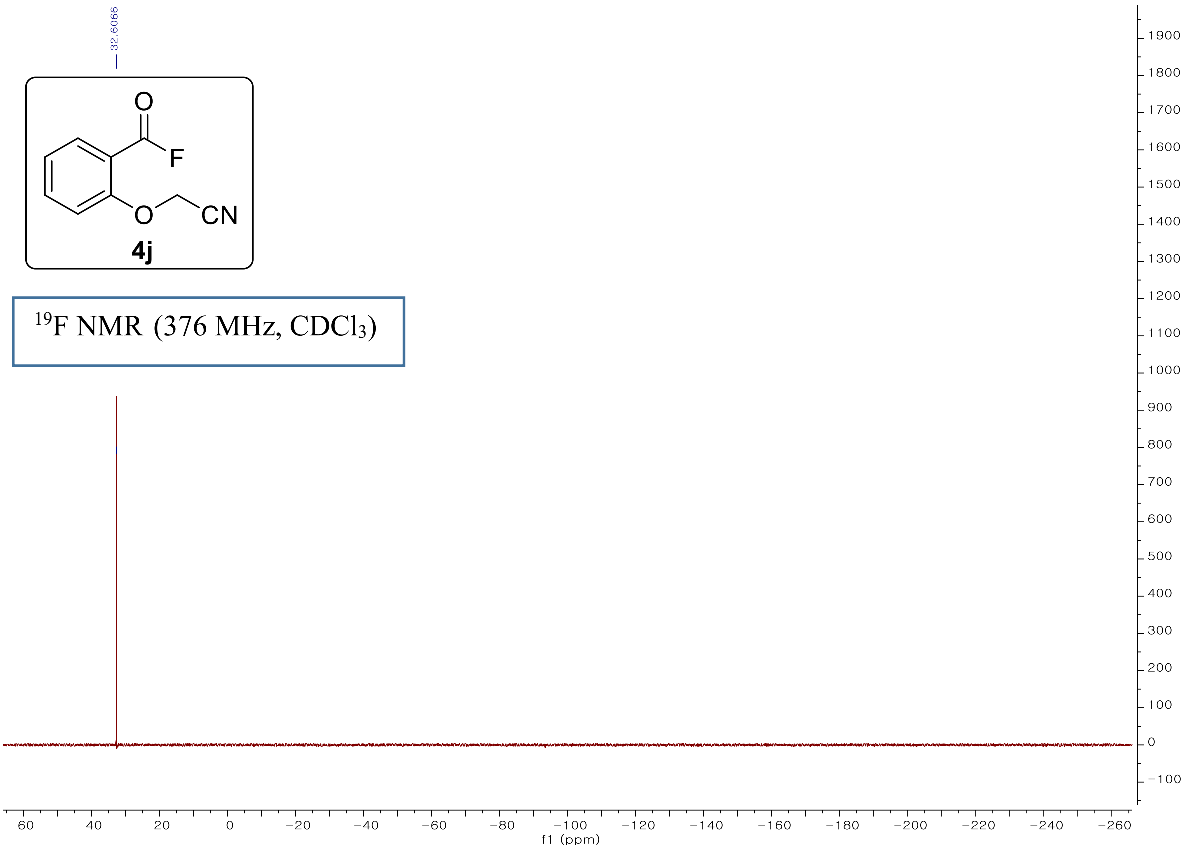
$^{19}$F NMR (376 MHz, CDCl$_3$)

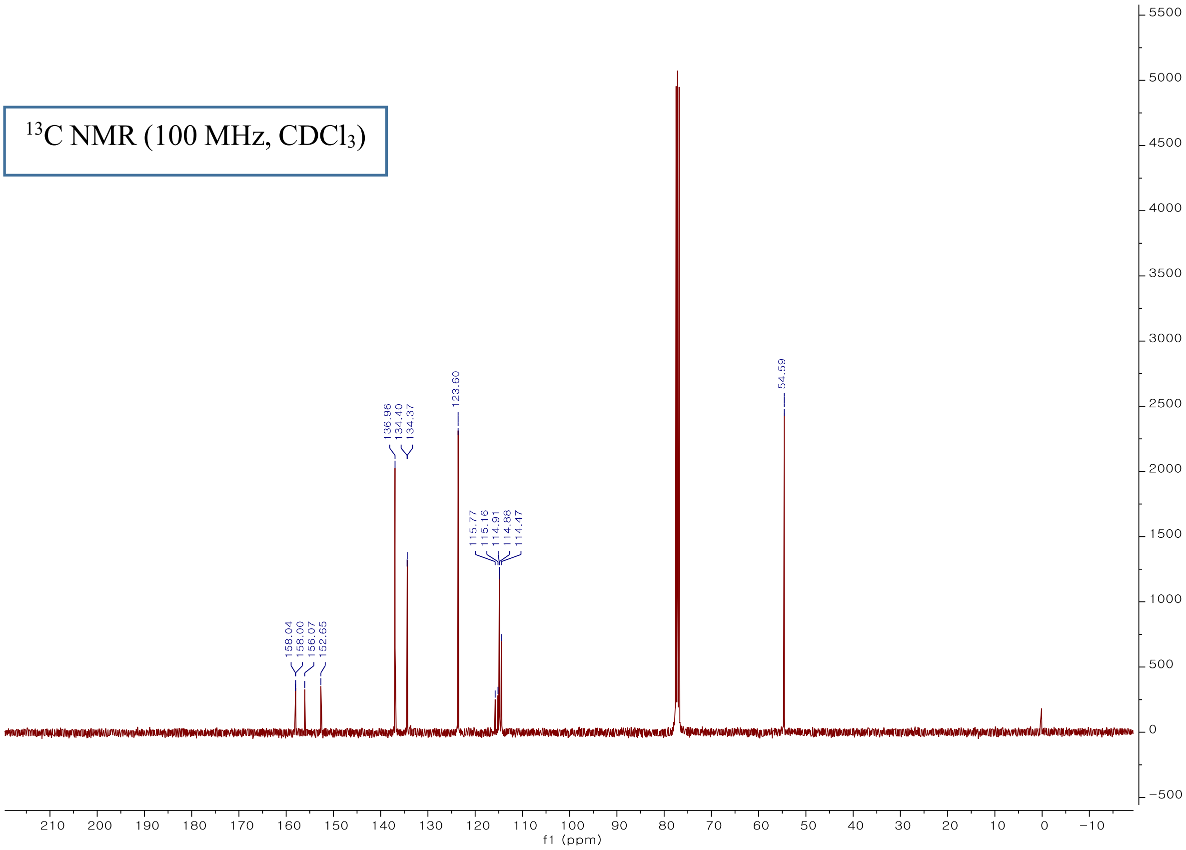


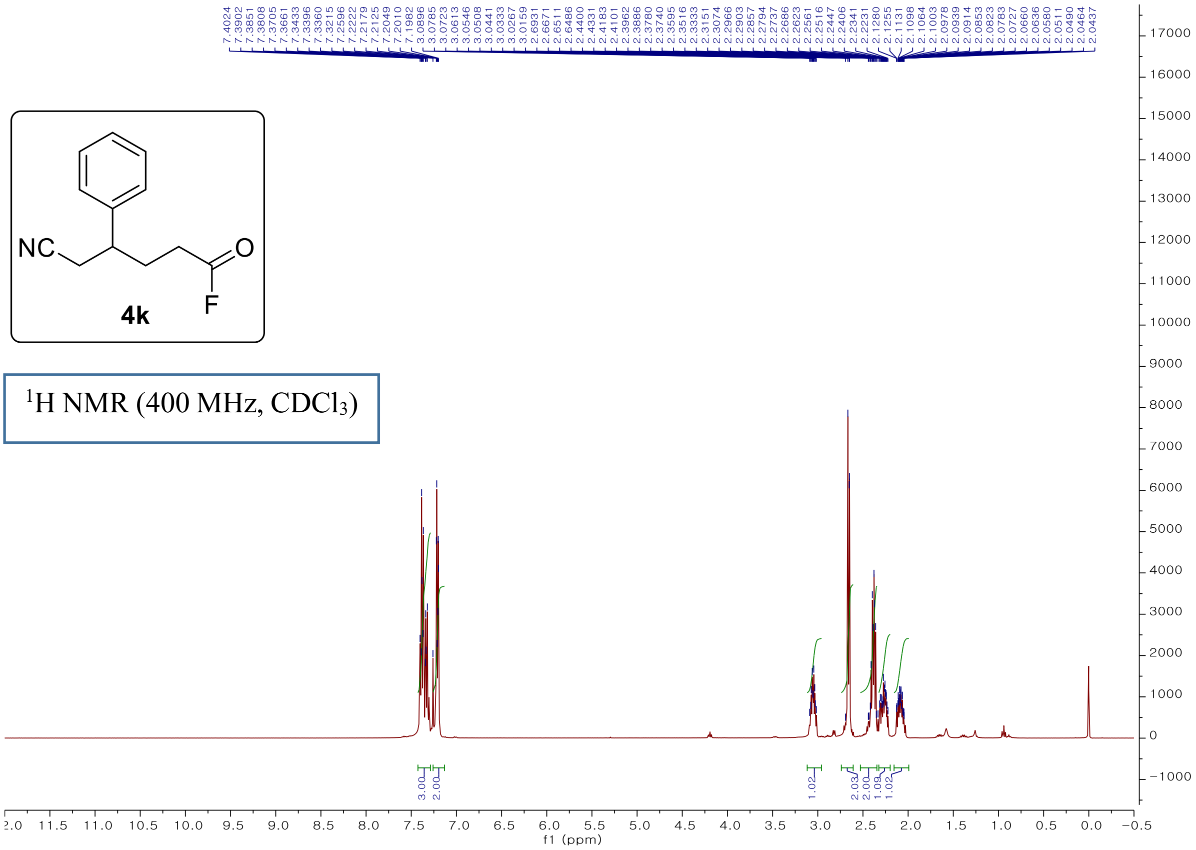
4i
13C NMR (100 MHz, CDCl3)
157.69
154.25
148.14
137.83
137.16
135.60
132.87
132.85
130.57
130.29
130.25
123.46
122.88
116.27
100.20
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



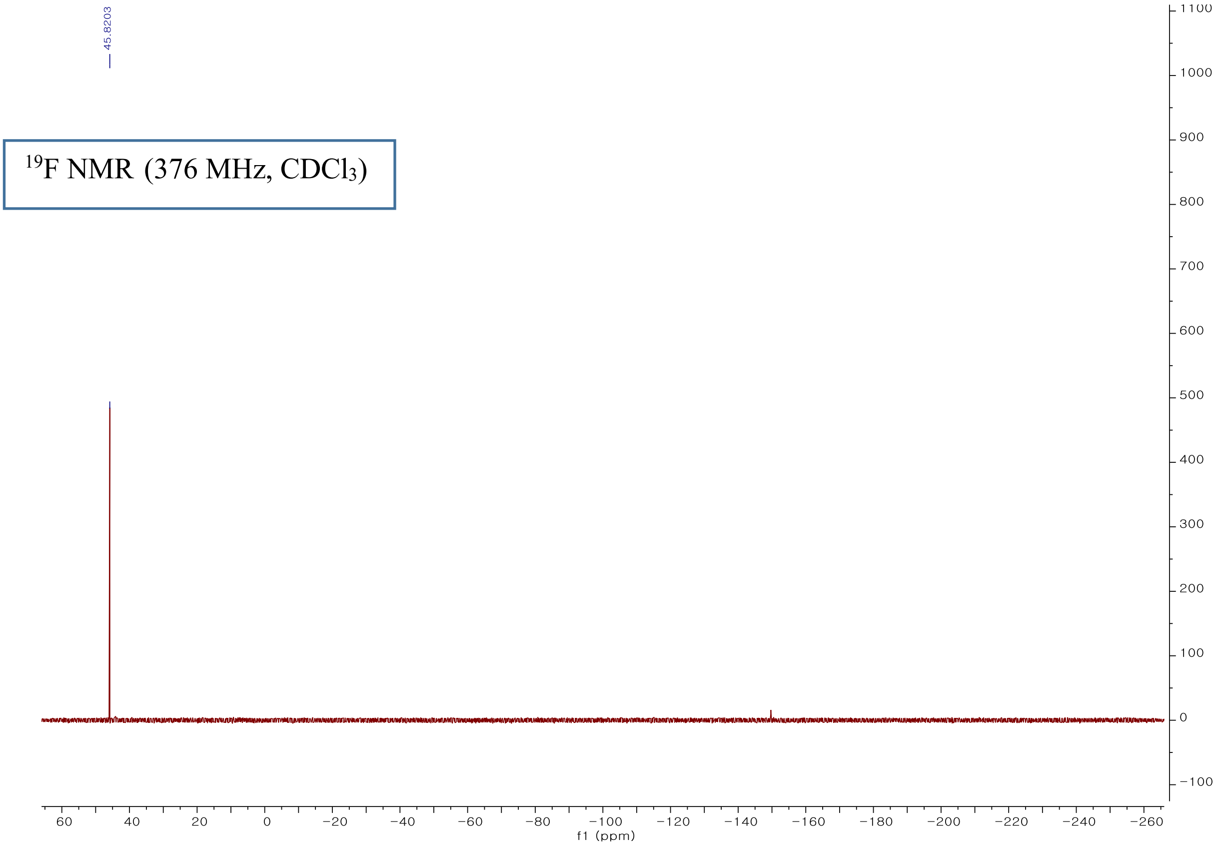
4j
1H NMR (400 MHz, CDCl3)
8.0444
8.0381
8.0241
8.0177
7.7706
7.7634
7.7492
7.7322
7.7238
7.2917
7.2805
7.2721
7.2210
7.2141
7.2002
7.1931
4.9517
1.00
1.01
1.06
1.00
2.09
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


32.6066
O
F
O
CN
4j
19F NMR (376 MHz, CDCl3)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
−260
f1 (ppm)

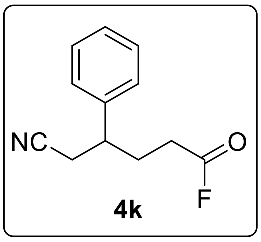

13C NMR (100 MHz, CDCl3)
158.04
158.00
156.07
152.65
136.96
134.40
134.37
123.60
115.77
115.16
114.91
114.88
114.47
54.59
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



$^1$H NMR (400 MHz, CDCl$_3$)

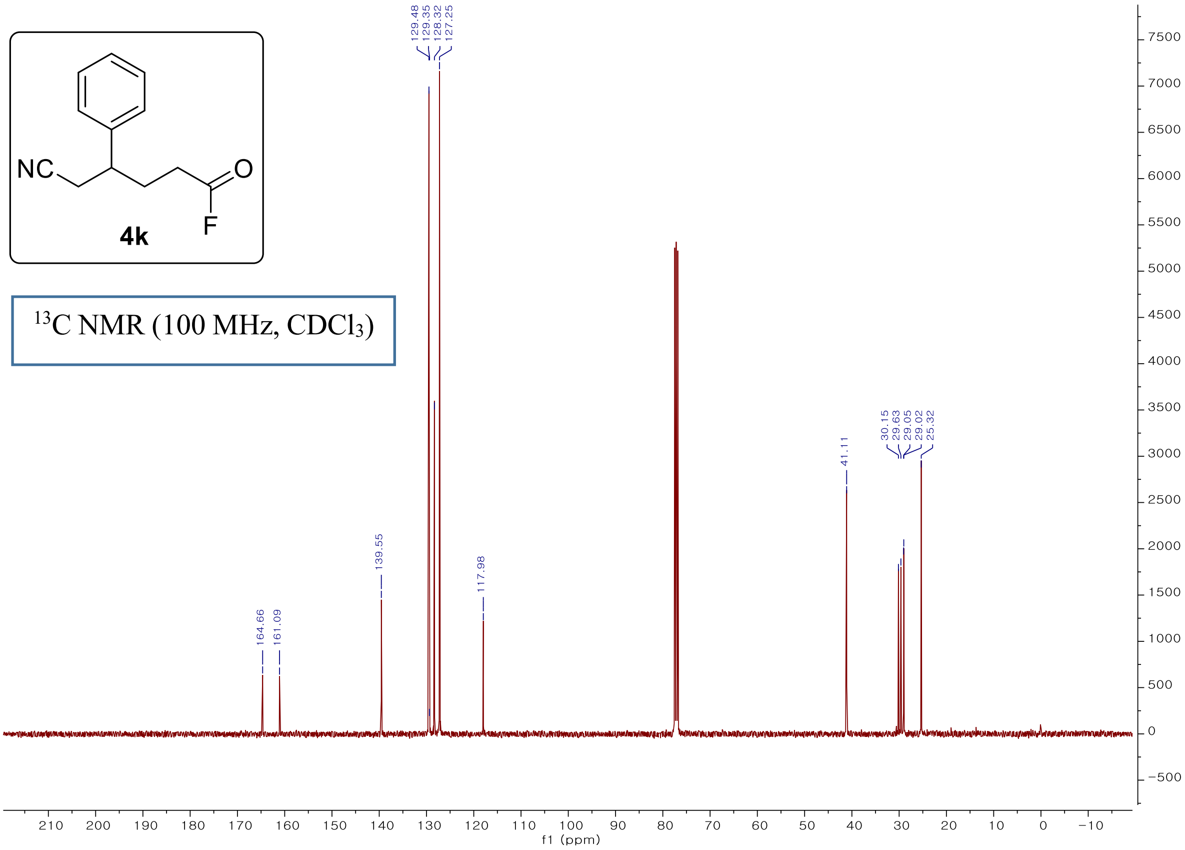


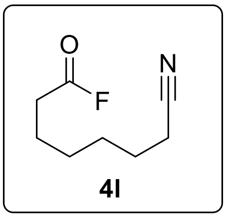
$^{19}$F NMR (376 MHz, CDCl$_3$)



**4k**

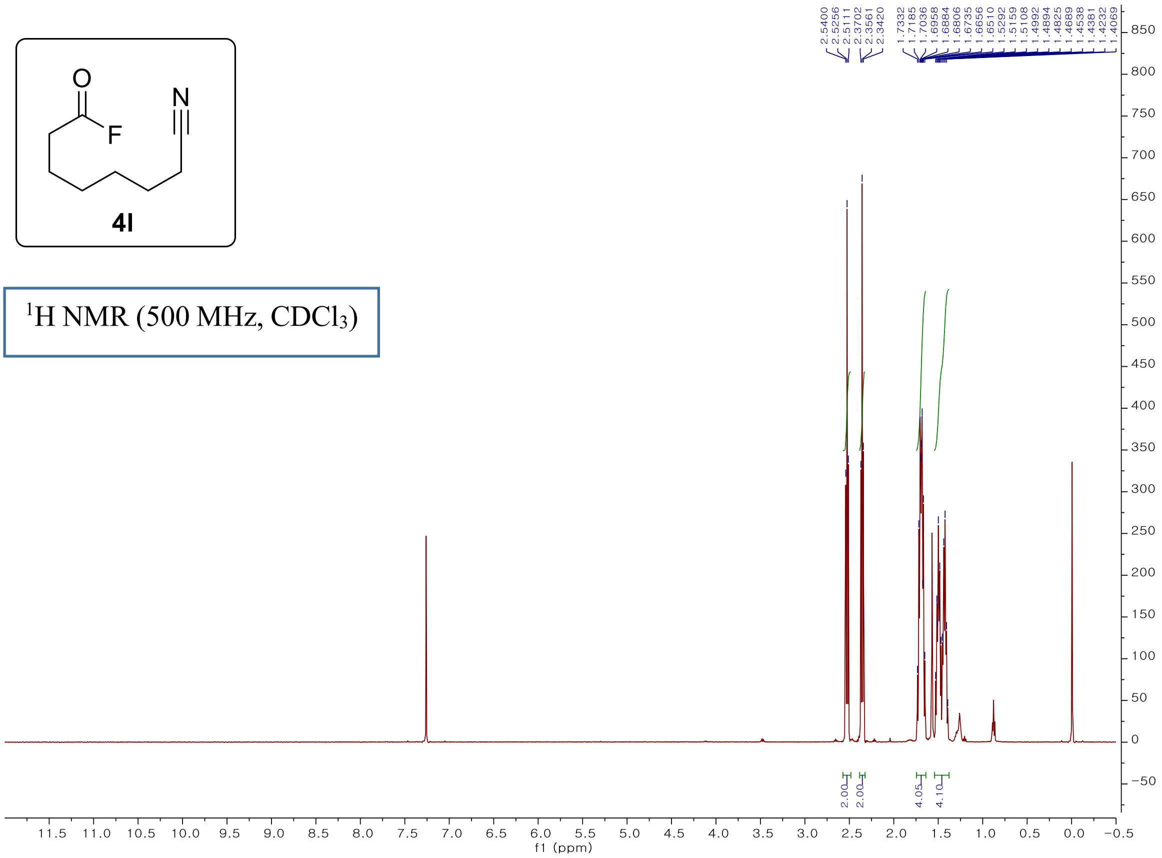
$^{13}$C NMR (100 MHz, CDCl$_3$)

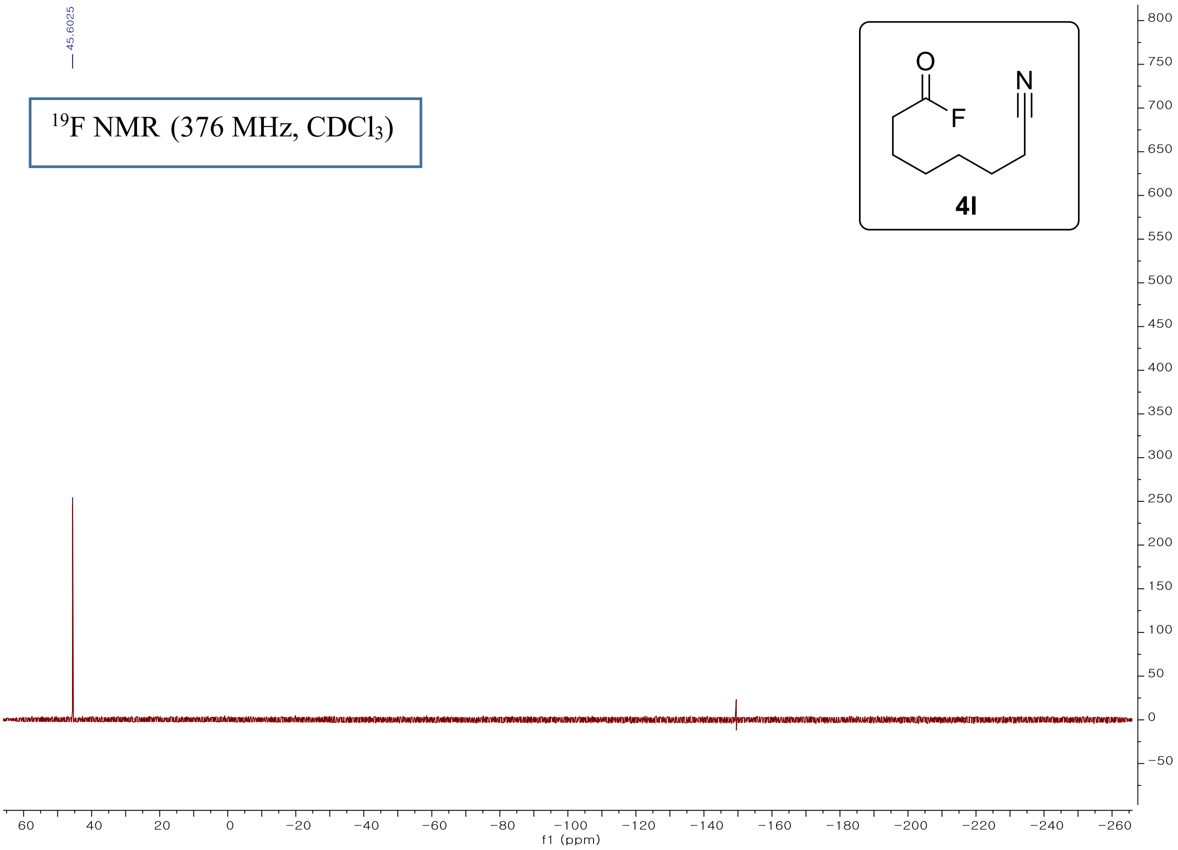


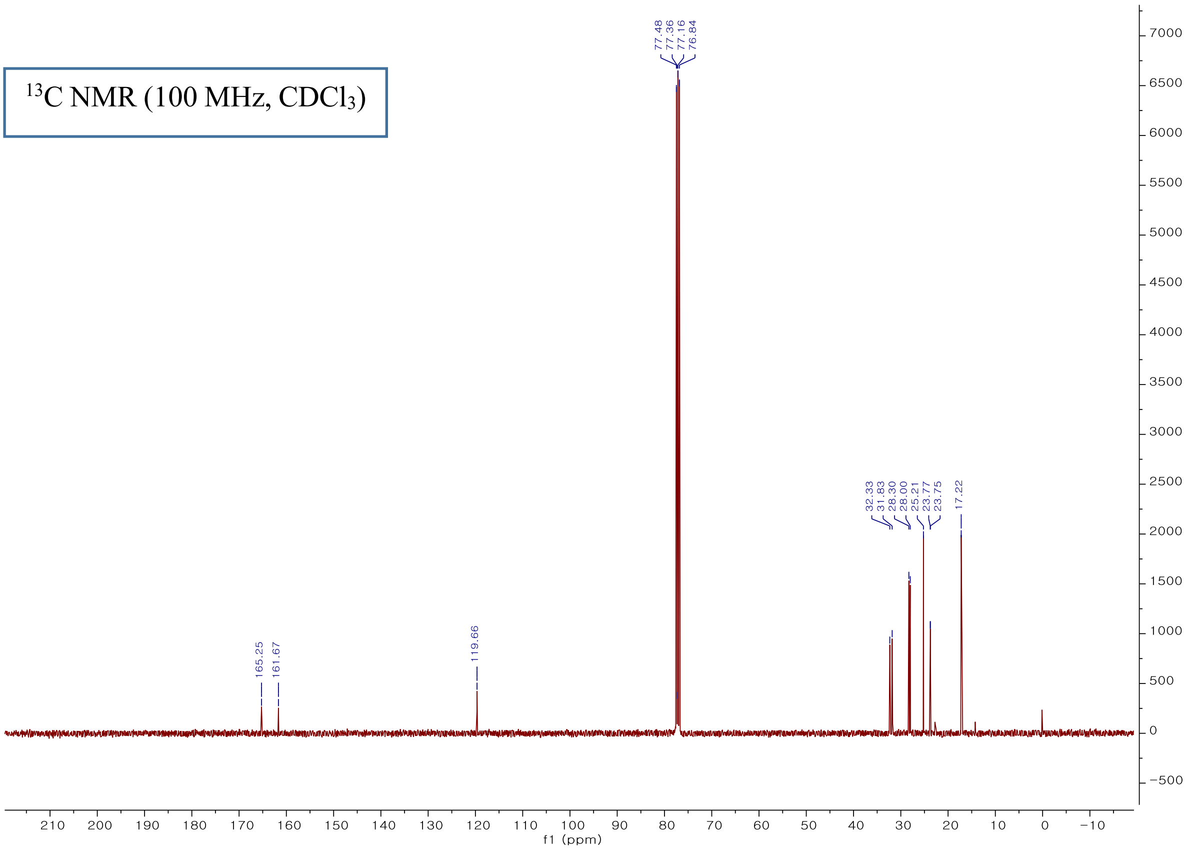


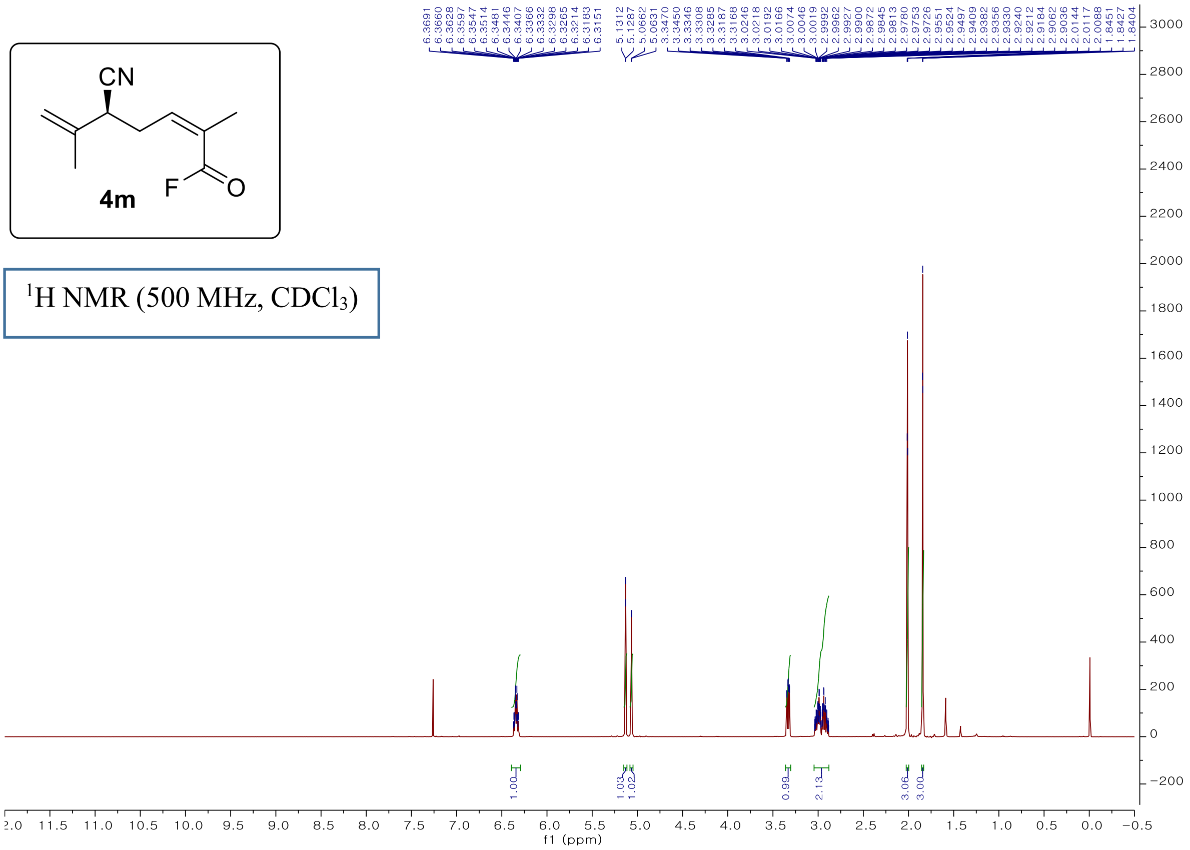
**4l**

$^{1}$H NMR (500 MHz, CDCl$_3$)

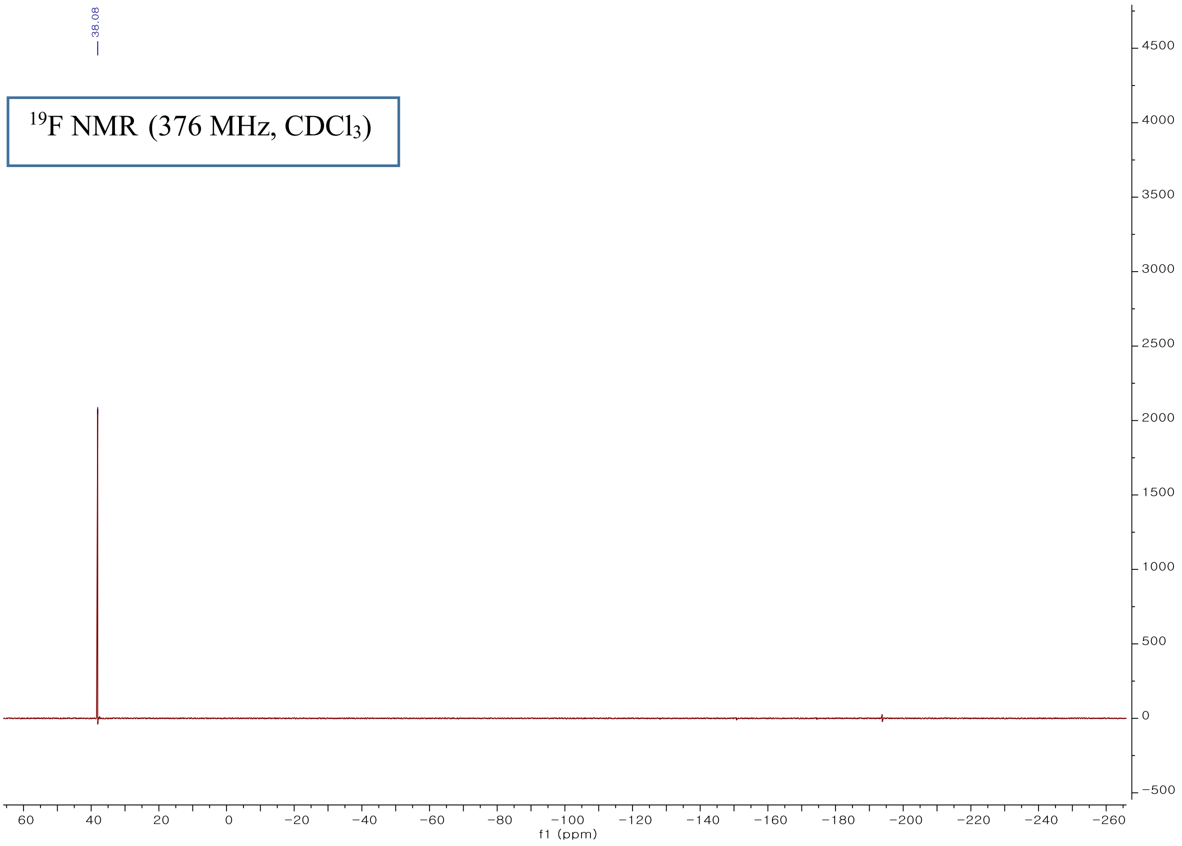


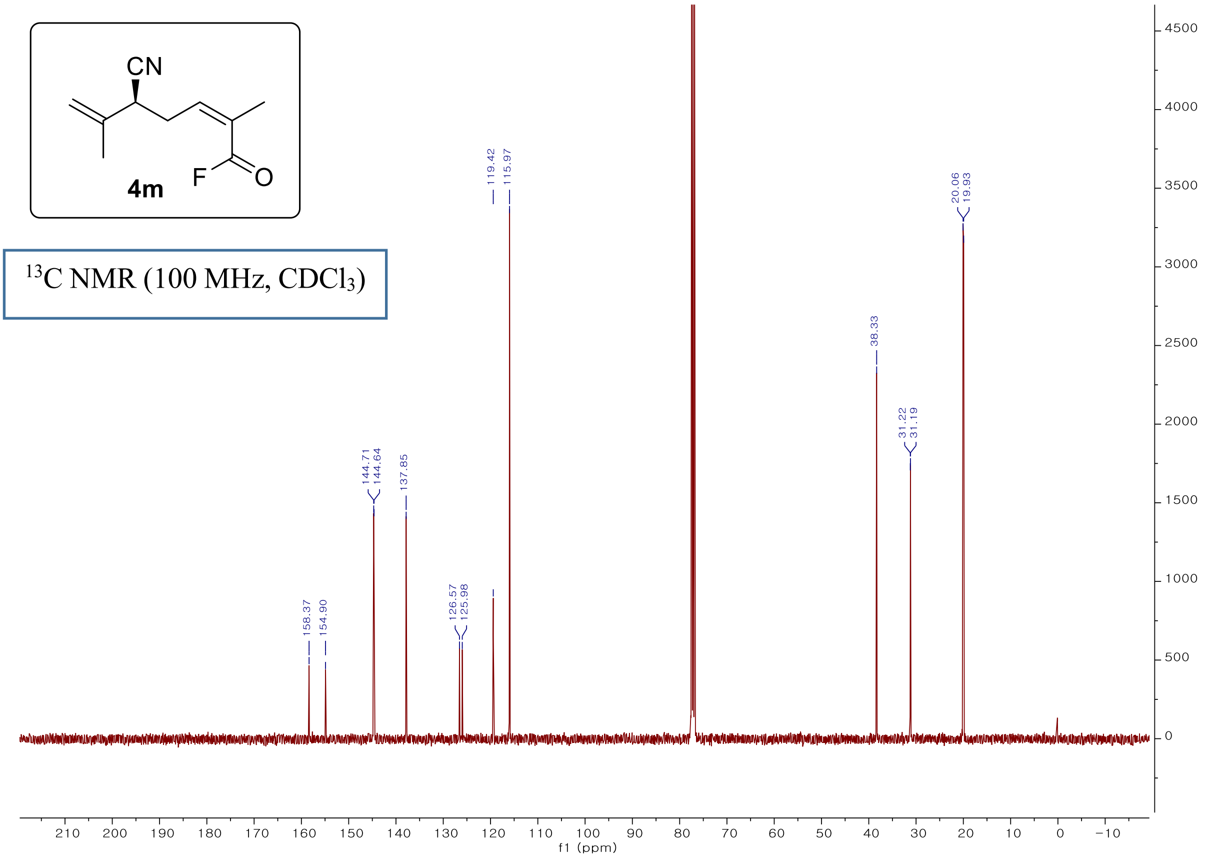

45.6025
$^{19}$F NMR (376 MHz, CDCl$_3$)
O
F
N
4l
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
−260
f1 (ppm)


77.48
77.36
77.16
76.84
$^{13}$C NMR (100 MHz, CDCl$_3$)
165.25
161.67
119.66
32.33
31.83
28.30
28.00
25.21
23.77
23.75
17.22
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


4m

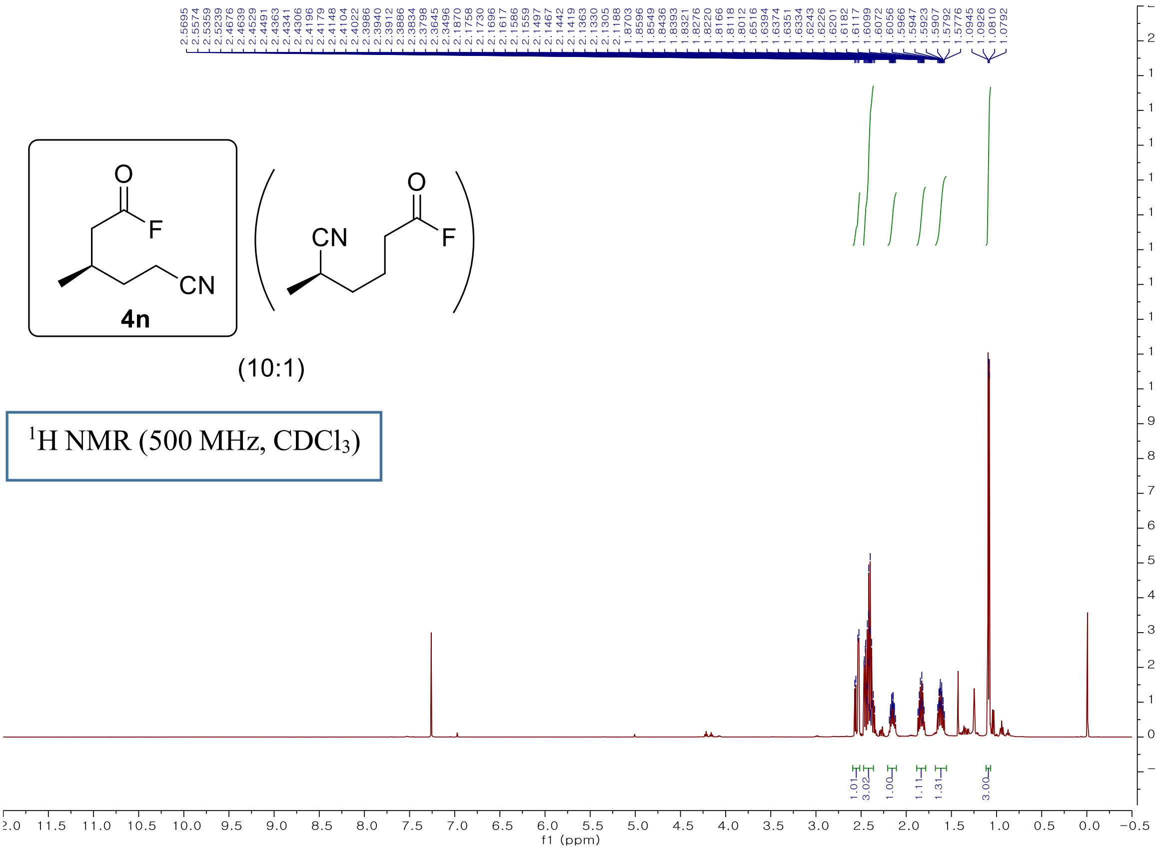
¹H NMR (500 MHz, $CDCl_3$)


¹⁹F NMR (376 MHz, $CDCl_3$)



**4m**

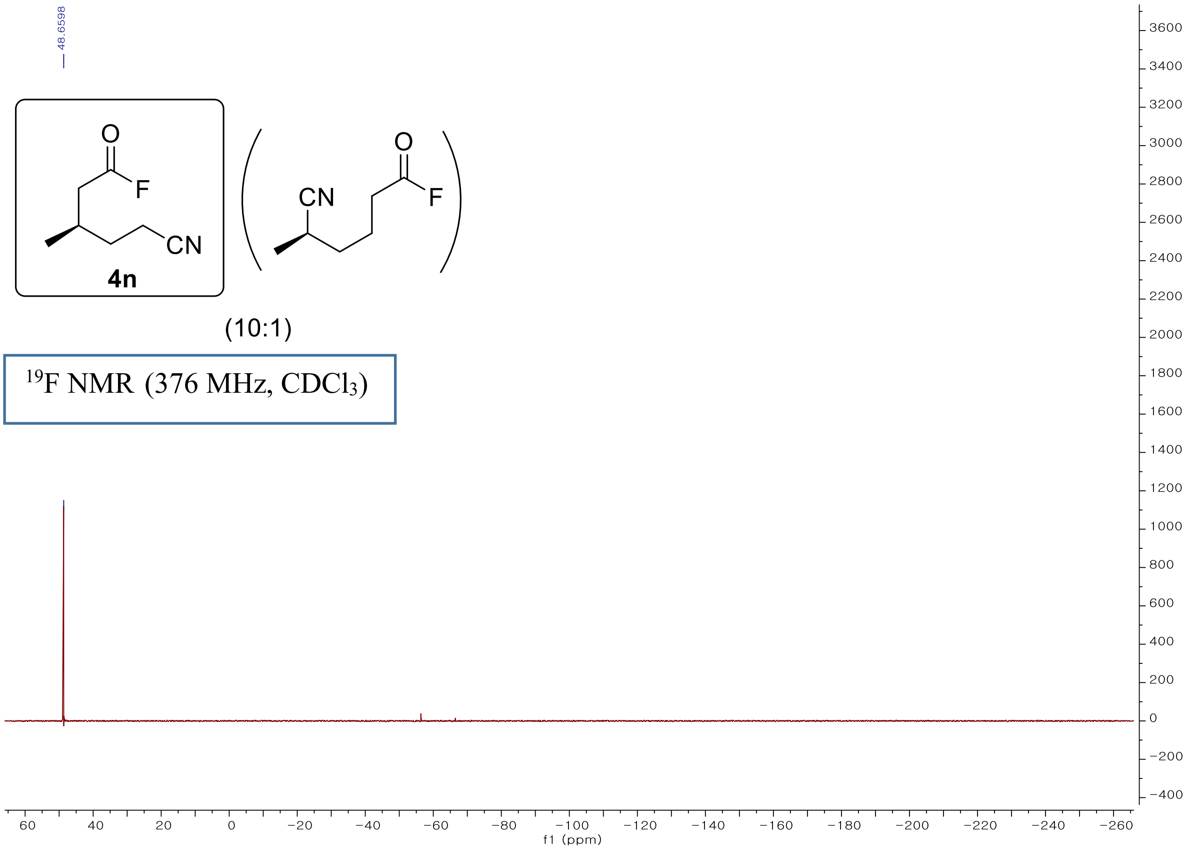
$^{13}$C NMR (100 MHz, CDCl$_3$)



**4n**

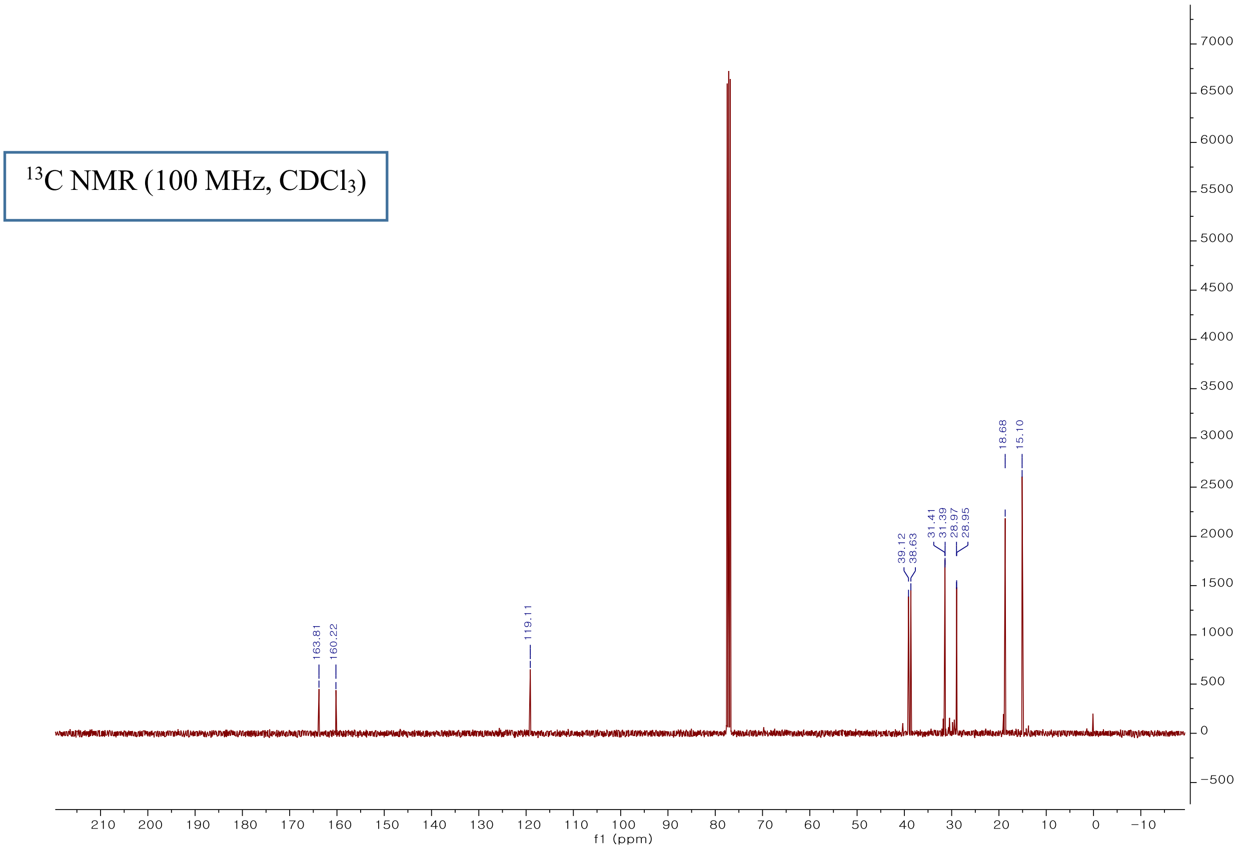
(10:1)

$^{1}$H NMR (500 MHz, CDCl$_3$)

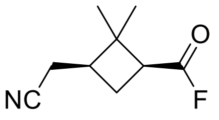


(10:1)

$^{19}$F NMR (376 MHz, $CDCl_3$)

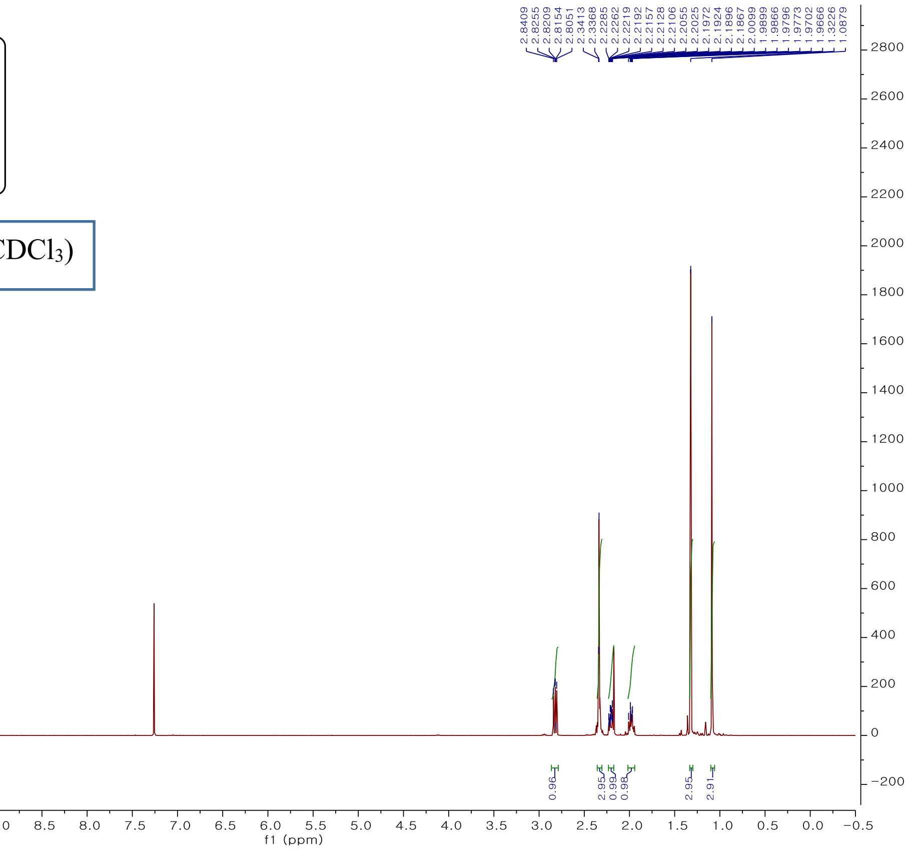


$^{13}$C NMR (100 MHz, $CDCl_3$)

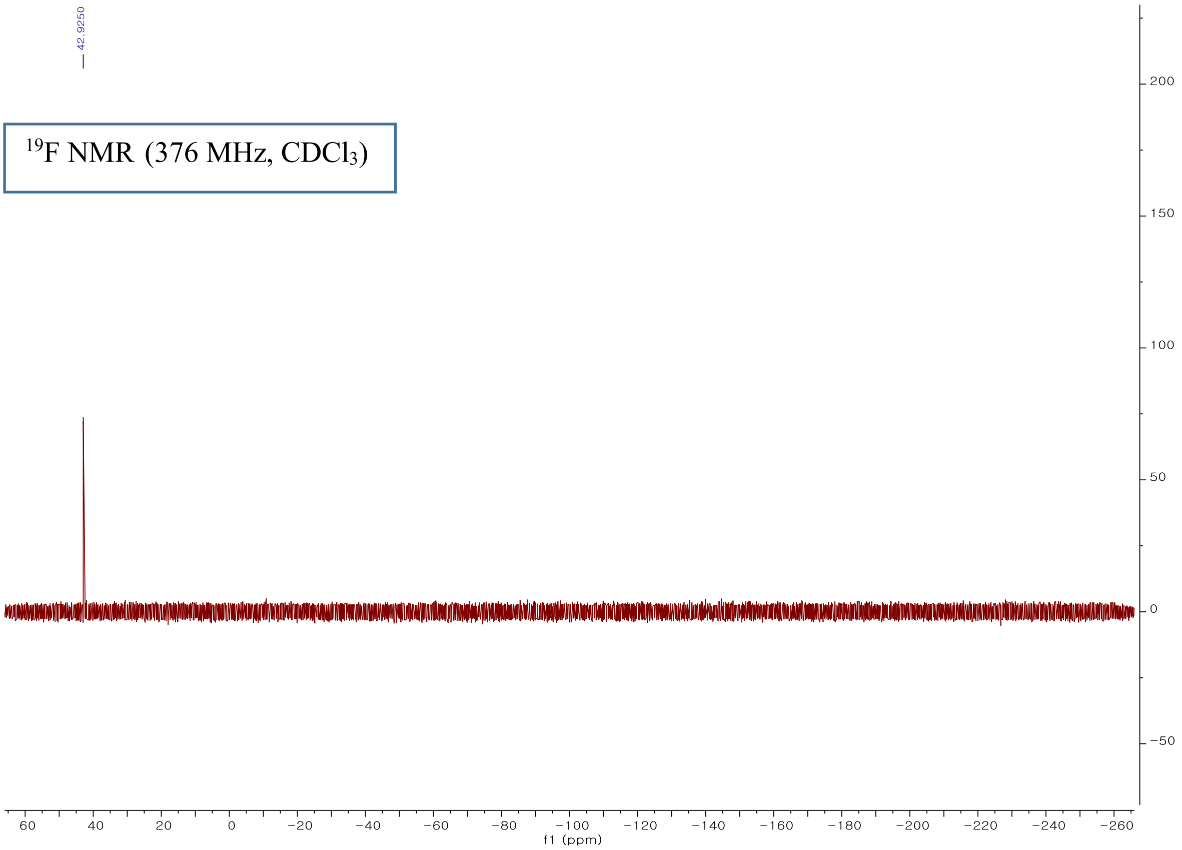


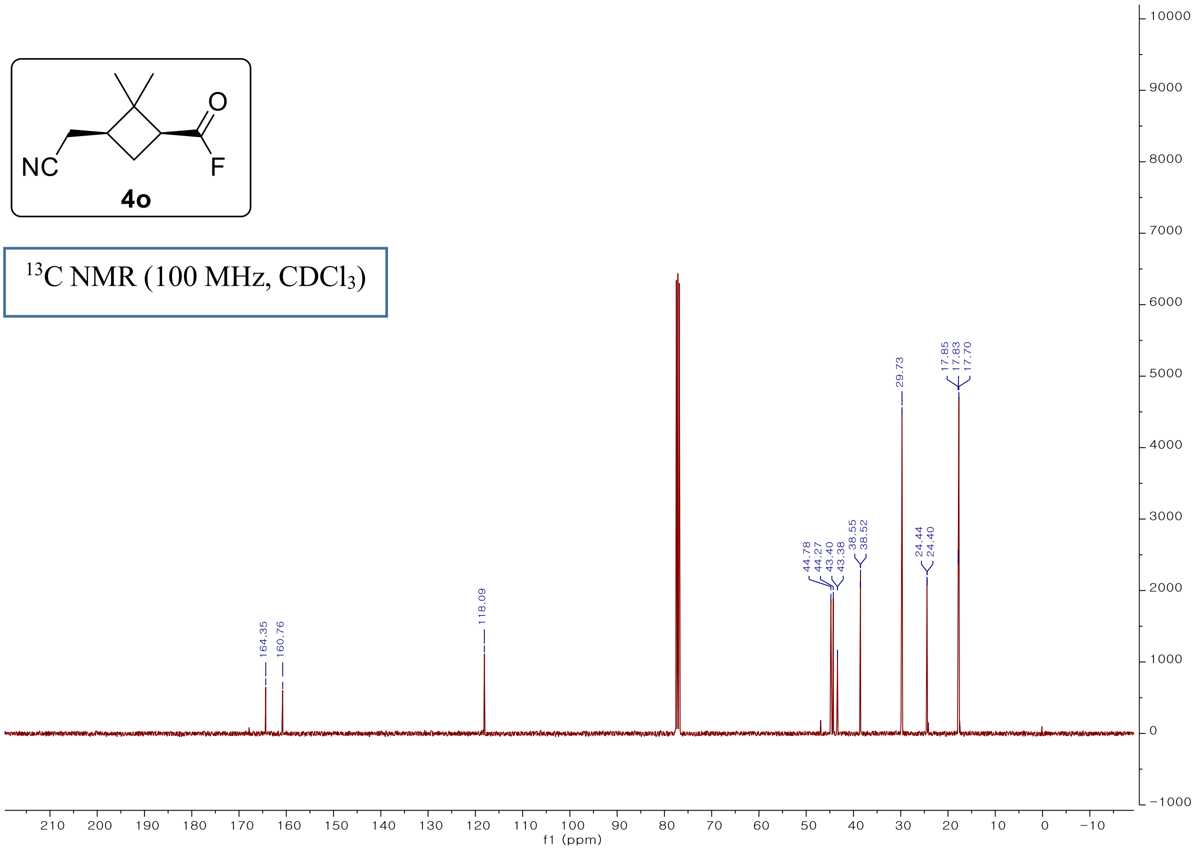
**4o**

$^{1}$H NMR (500 MHz, $CDCl_3$)



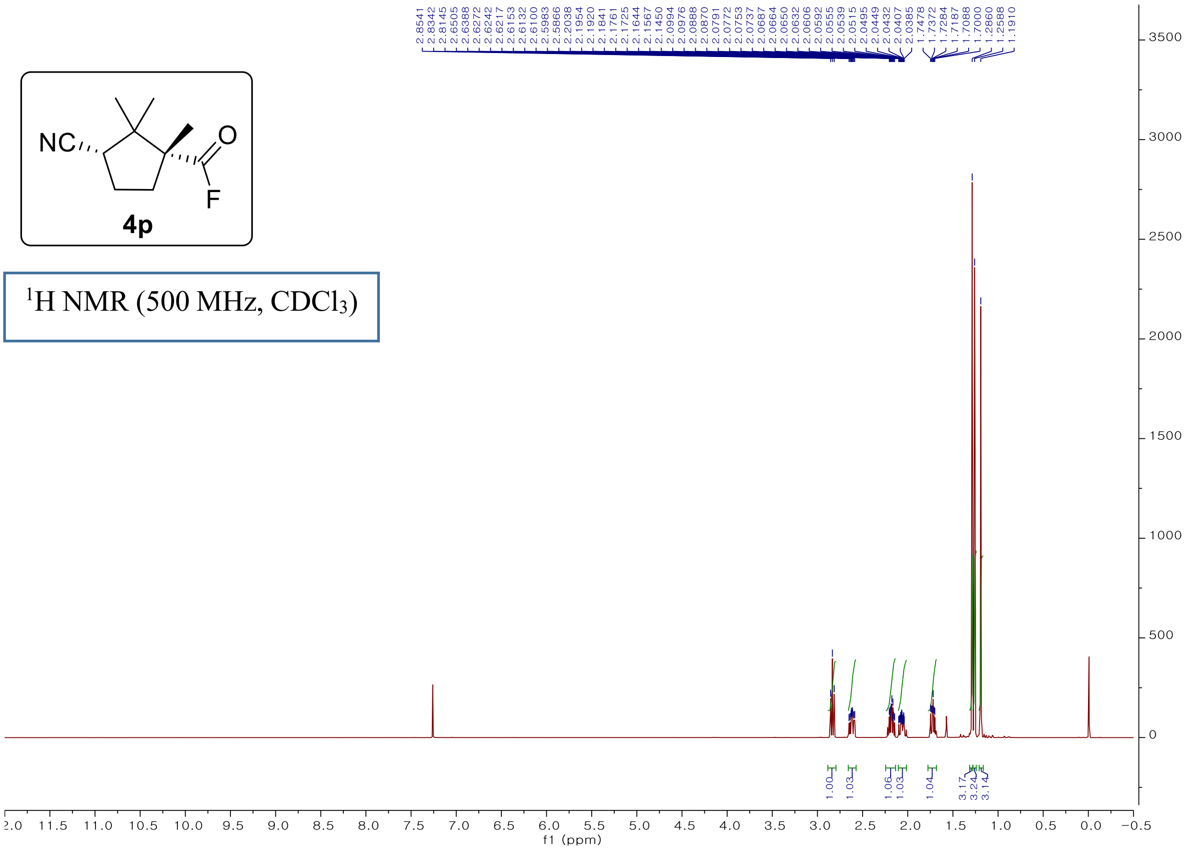
$^{19}$F NMR (376 MHz, $CDCl_3$)





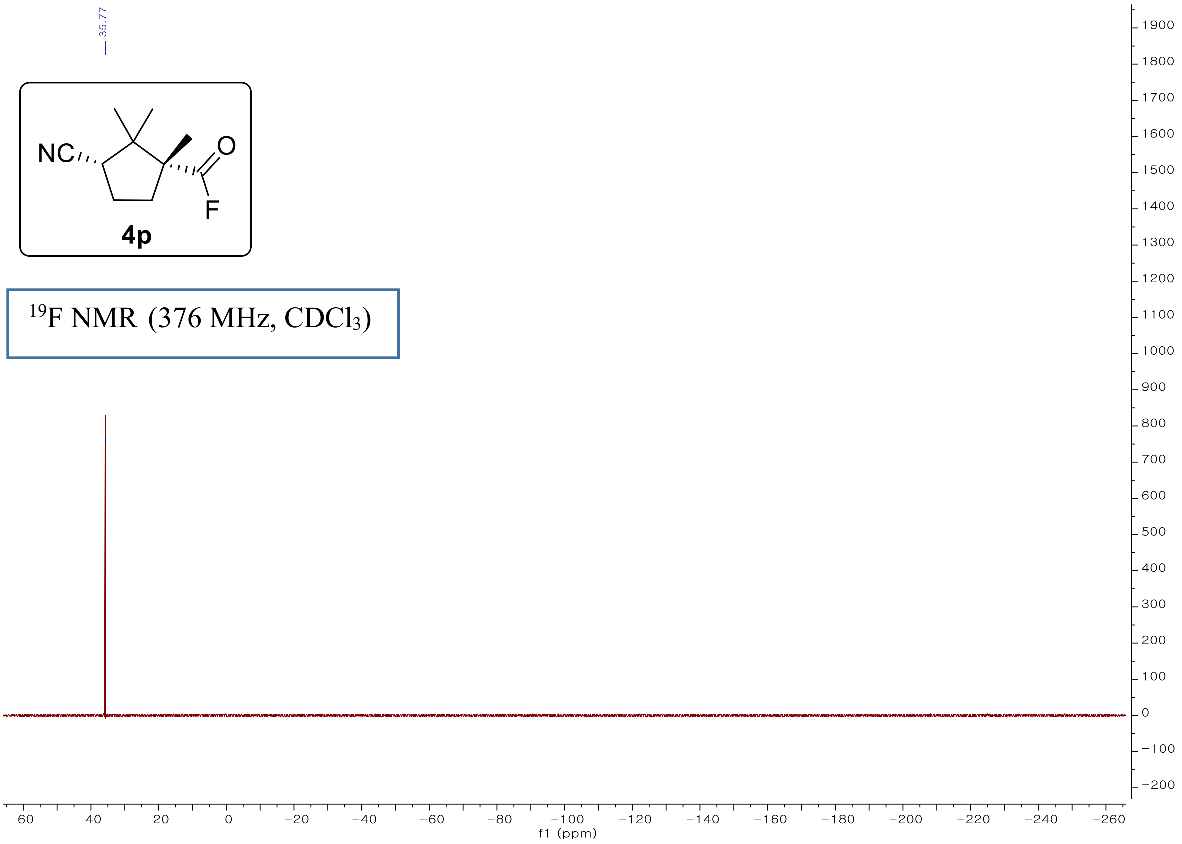
**4o**

$^{13}$C NMR (100 MHz, CDCl$_3$)



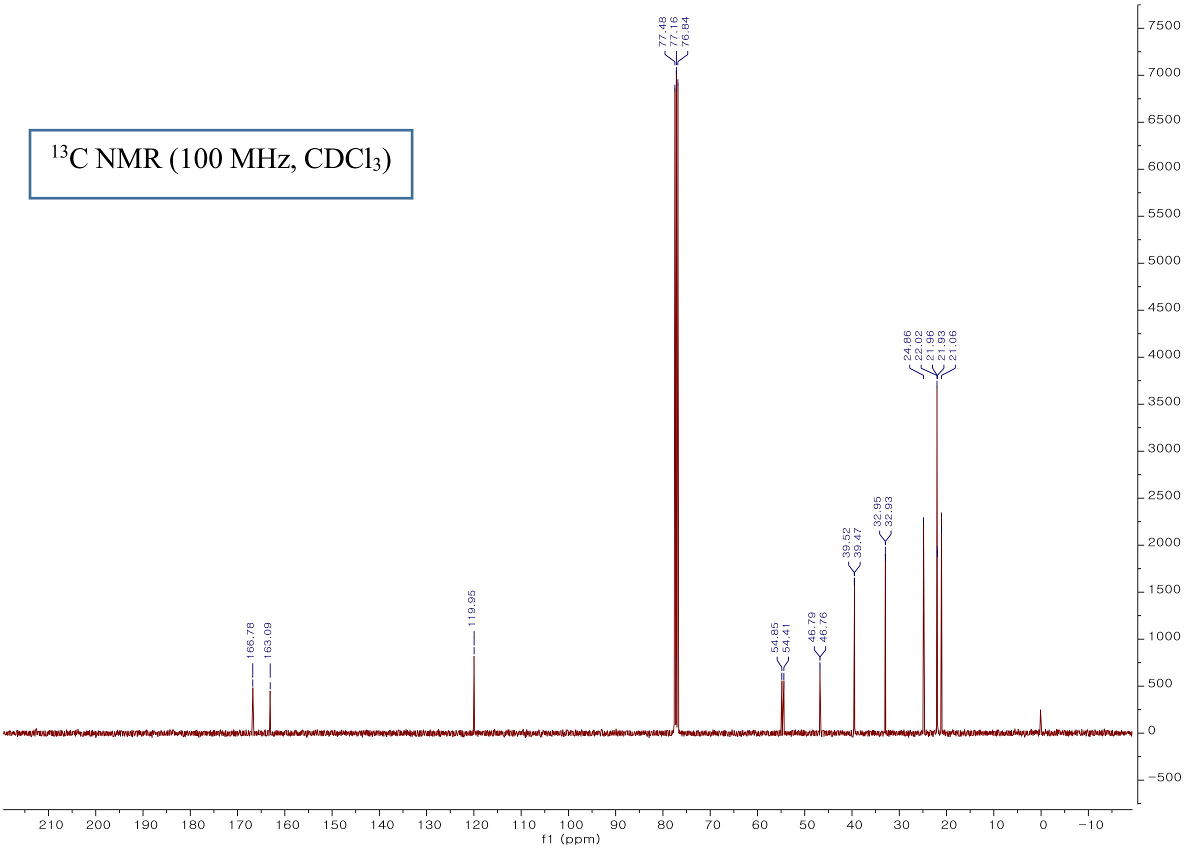
**4p**

$^1$H NMR (500 MHz, CDCl$_3$)

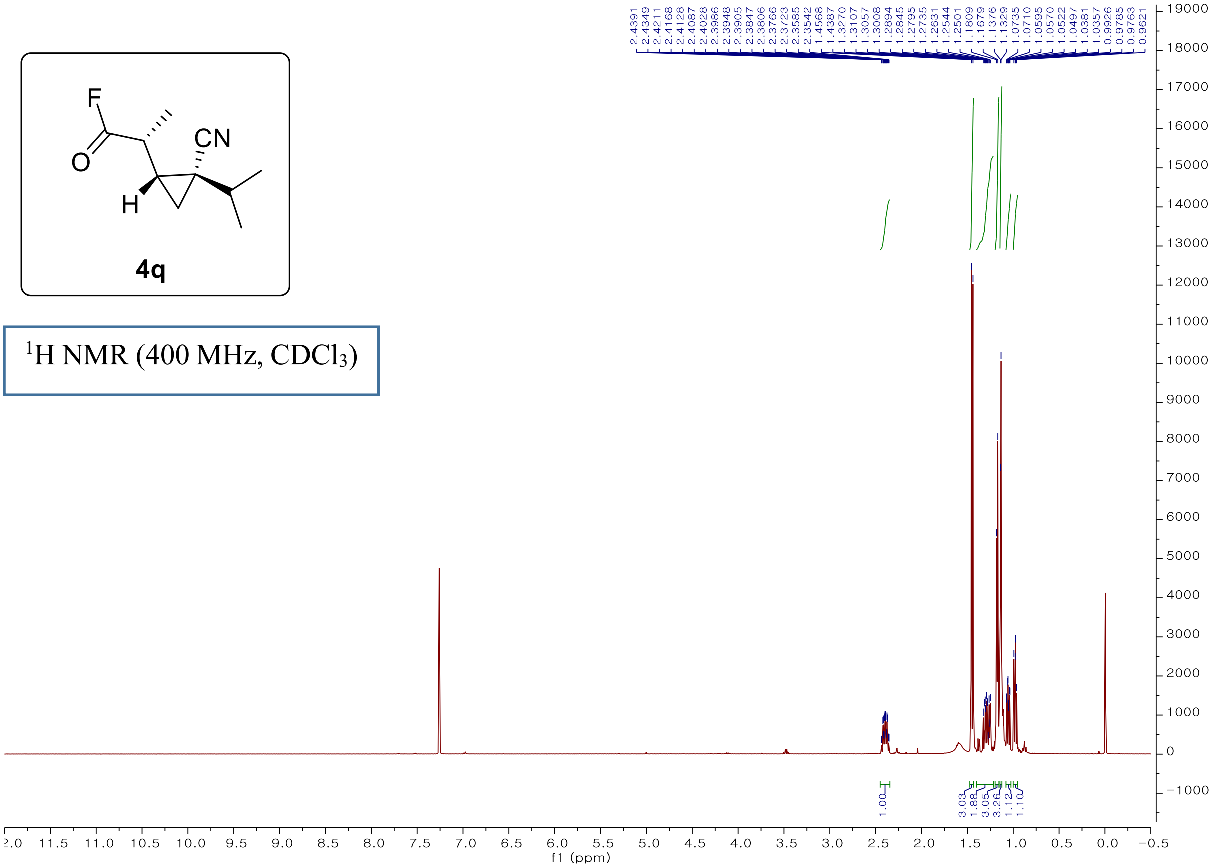


**4p**

$^{19}$F NMR (376 MHz, CDCl$_3$)



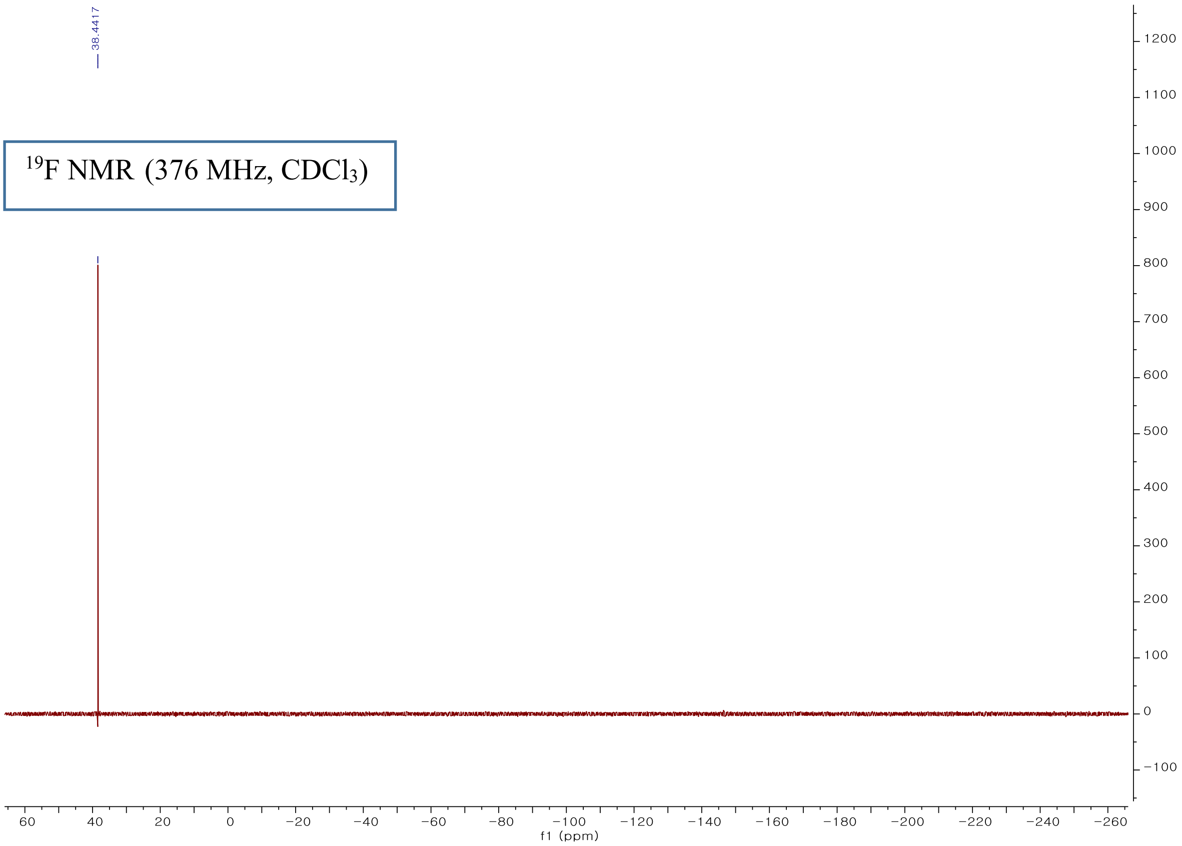
$^{13}$C NMR (100 MHz, CDCl$_3$)

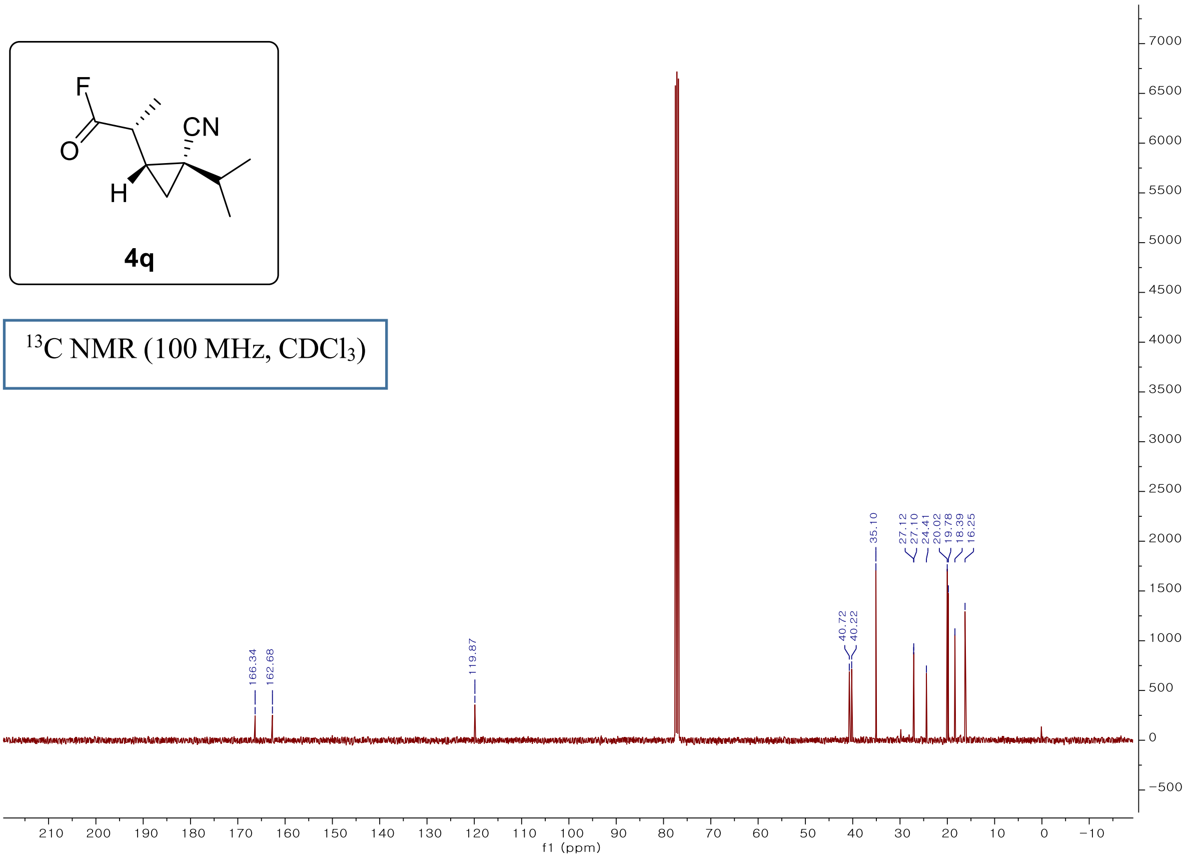


**4q**

$^{1}$H NMR (400 MHz, CDCl$_3$)

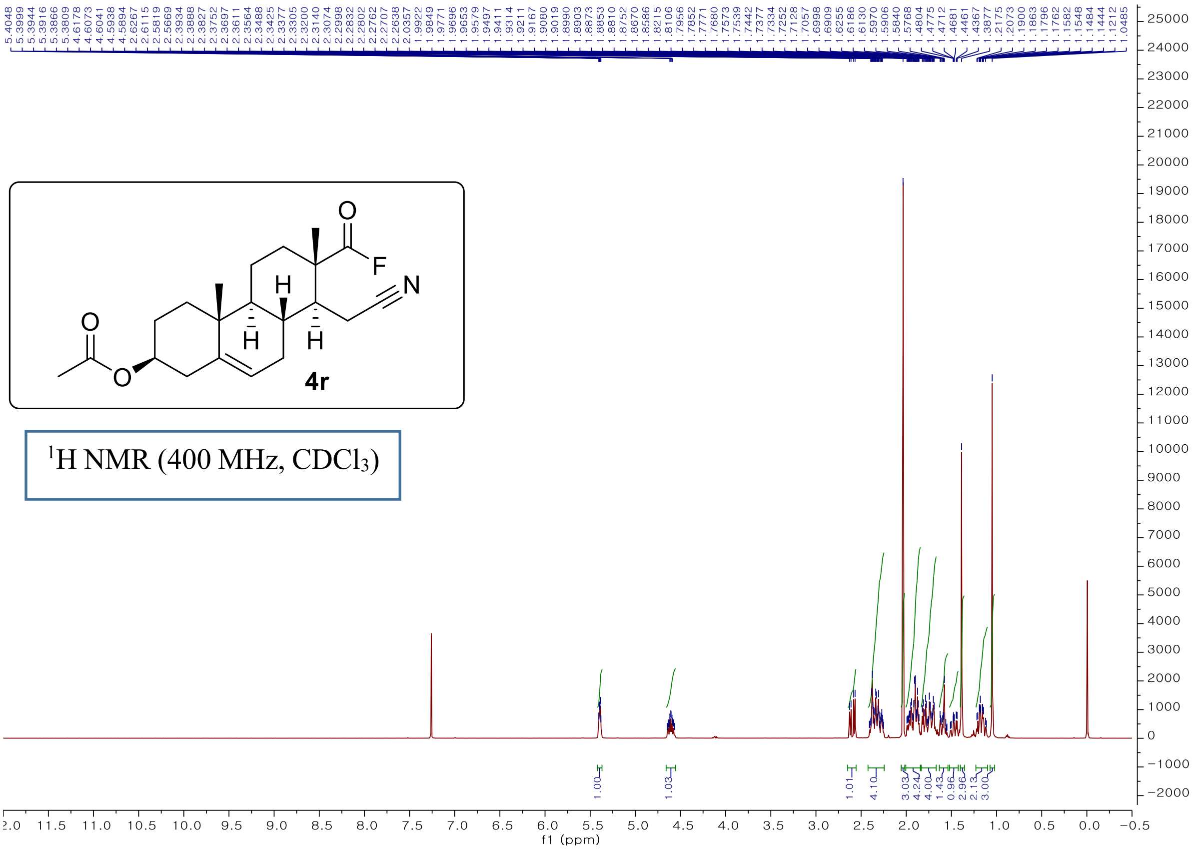
$^{19}$F NMR (376 MHz, CDCl$_3$)





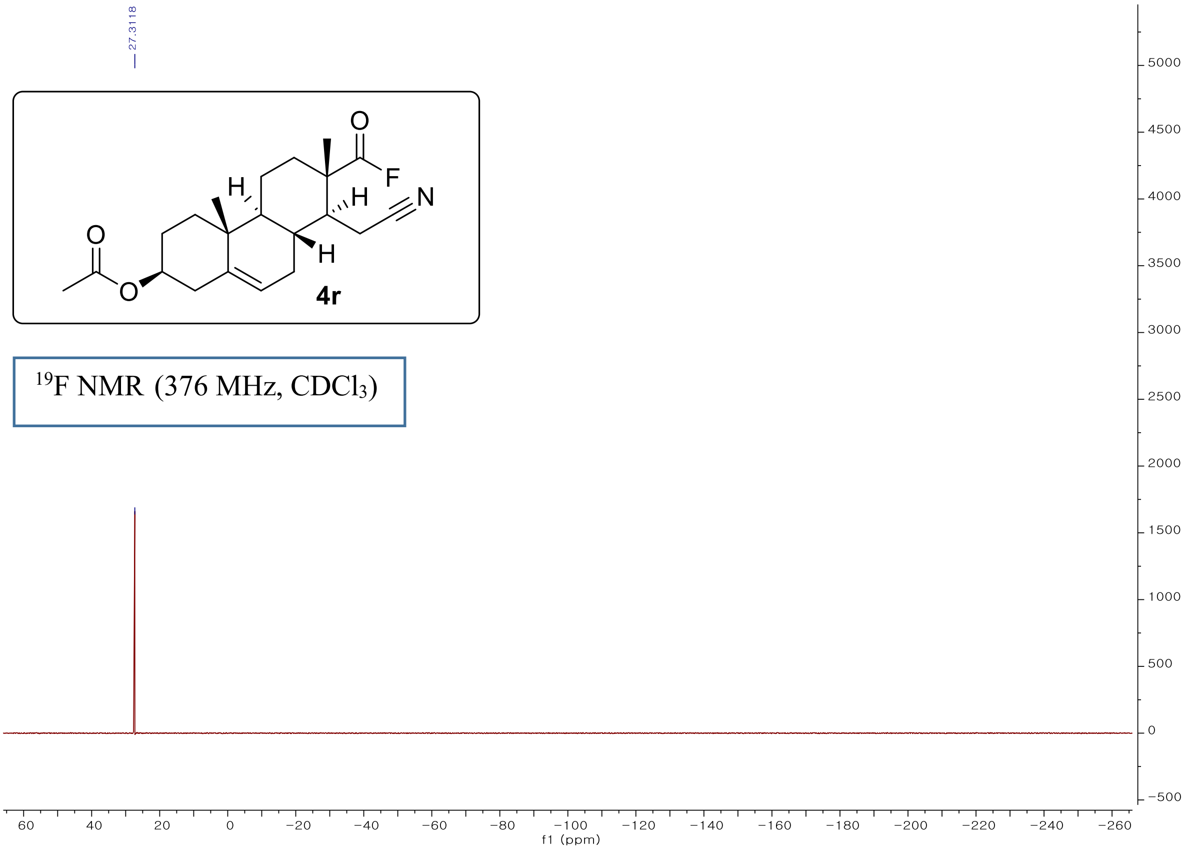
**4q**

$^{13}$C NMR (100 MHz, CDCl$_3$)

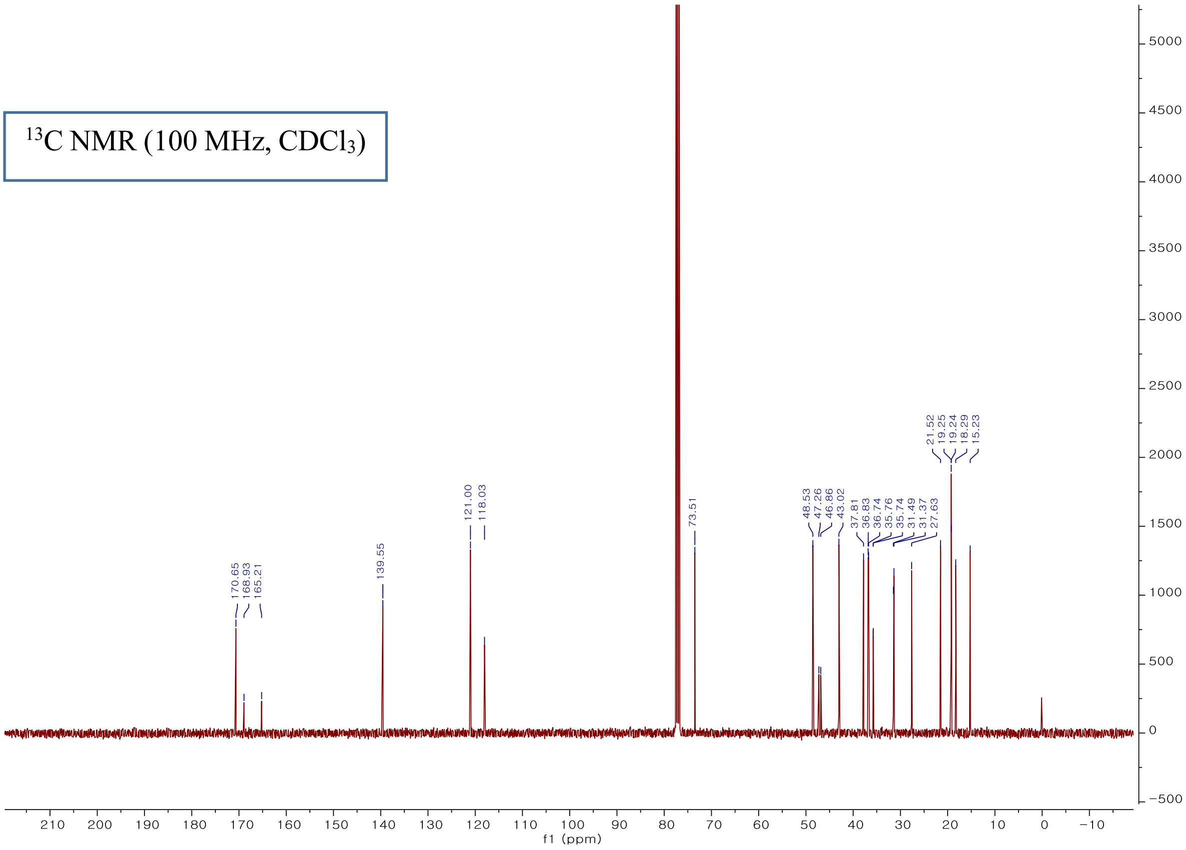


**4r**

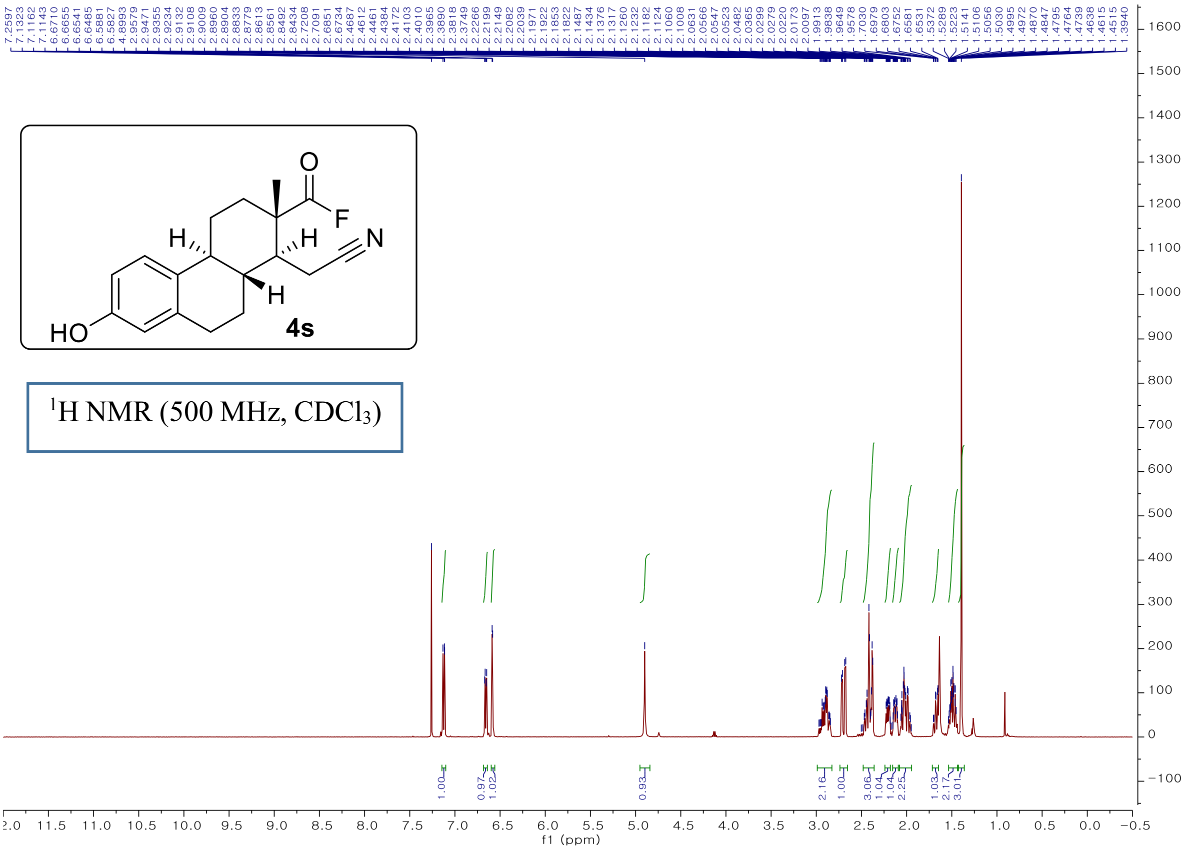
$^1$H NMR (400 MHz, CDCl$_3$)

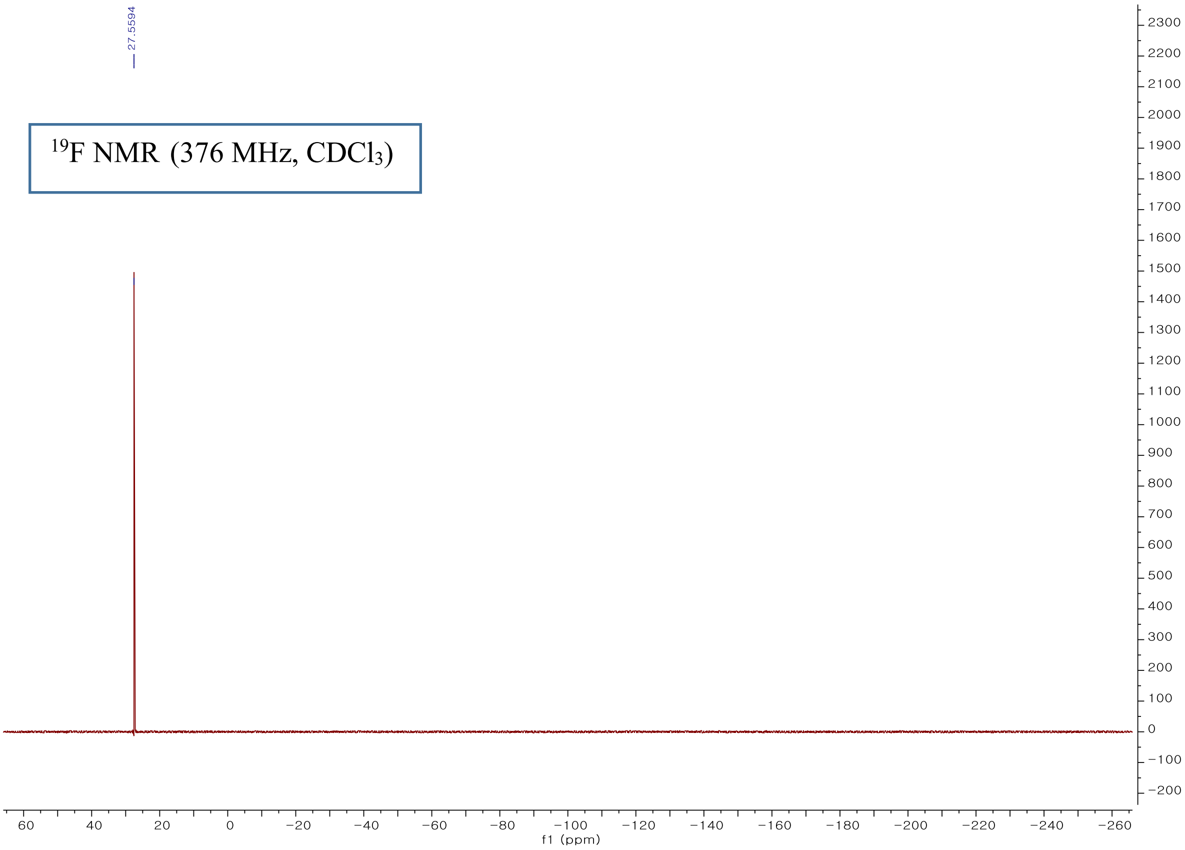


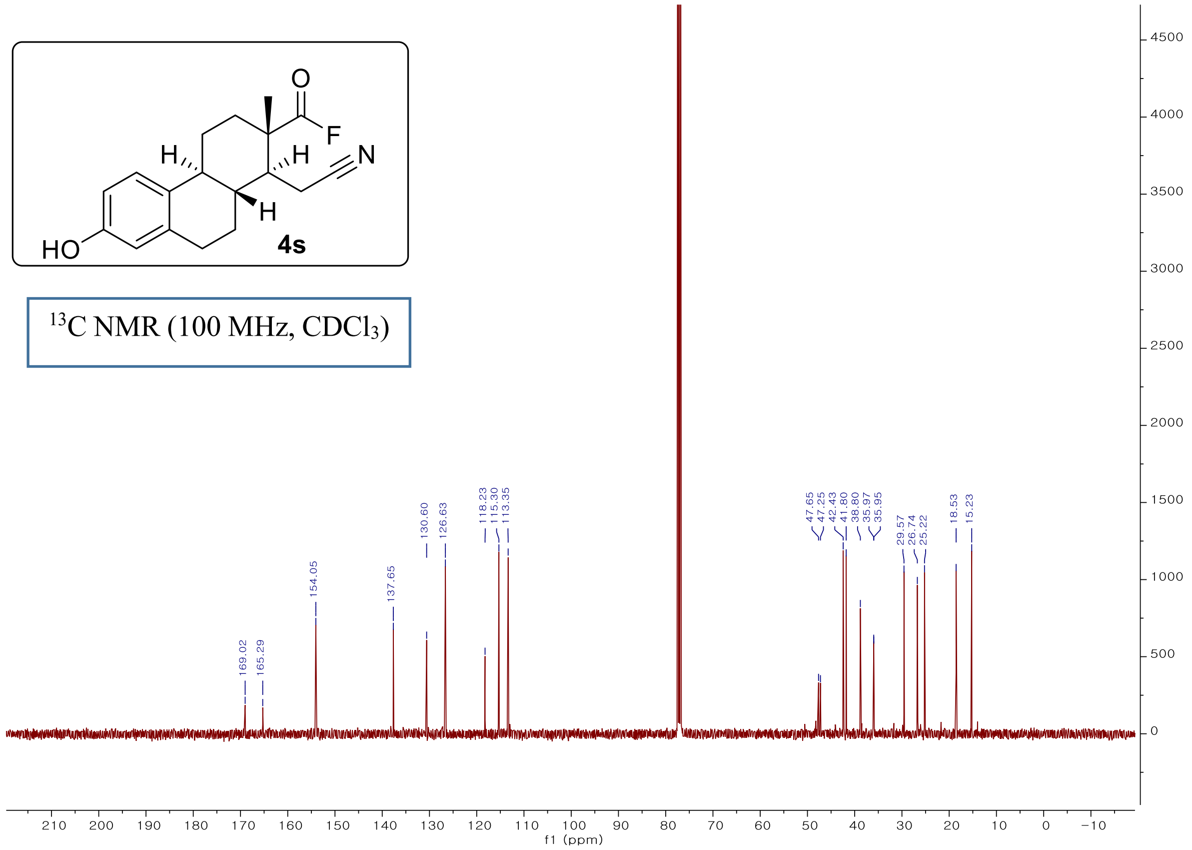
$^{19}$F NMR (376 MHz, CDCl$_3$)



$^{13}$C NMR (100 MHz, CDCl$_3$)

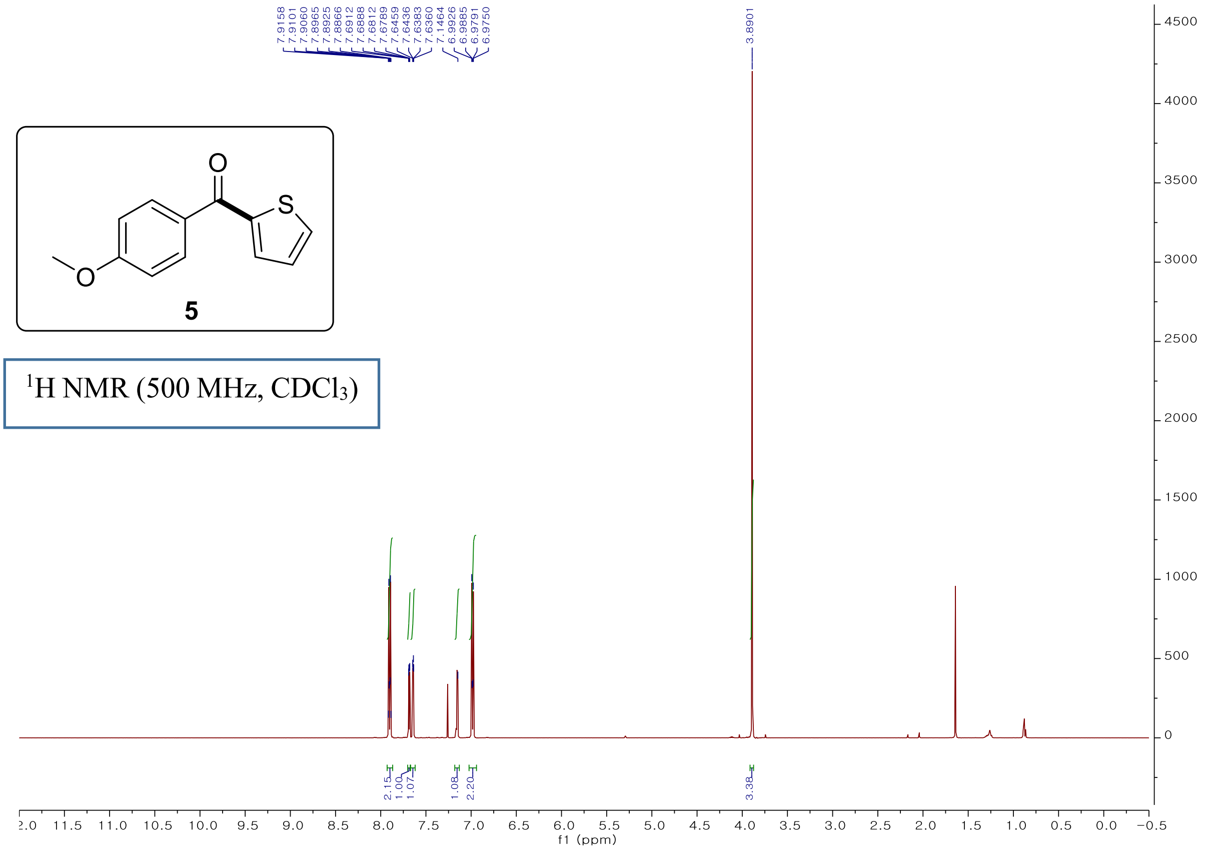

7.2597
7.1323
7.1162
7.1143
6.6710
6.6655
6.6541
6.6485
6.5881
6.5827
4.8993
2.9579
2.9471
2.9355
2.9234
2.9132
2.9108
2.9009
2.8960
2.8904
2.8833
2.8779
2.8613
2.8561
2.8492
2.8434
2.7208
2.7091
2.6851
2.6734
2.4687
2.4612
2.4461
2.4384
2.4172
2.4103
2.4010
2.3965
2.3890
2.3818
2.3749
2.2266
2.2199
2.2149
2.2082
2.2039
2.1971
2.1922
2.1853
2.1822
2.1487
2.1434
2.1376
2.1317
2.1260
2.1232
2.1182
2.1124
2.1060
2.1008
2.0631
2.0566
2.0547
2.0523
2.0482
2.0365
2.0299
2.0279
2.0220
2.0173
2.0097
1.9913
1.9838
1.9649
1.9578
1.7030
1.6979
1.6803
1.6752
1.6581
1.6531
1.5372
1.5289
1.5223
1.5141
1.5106
1.5056
1.5030
1.4995
1.4972
1.4870
1.4847
1.4795
1.4764
1.4739
1.4638
1.4615
1.4515
1.3940
O
F
H
H
N
H
HO
4s
$^1$H NMR (500 MHz, CDCl$_3$)
1.00
0.97
1.02
0.93
2.16
1.00
3.06
1.04
1.04
2.25
1.03
2.17
3.01
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100


27.5594
$^{19}$F NMR (376 MHz, CDCl$_3$)
f1 (ppm)



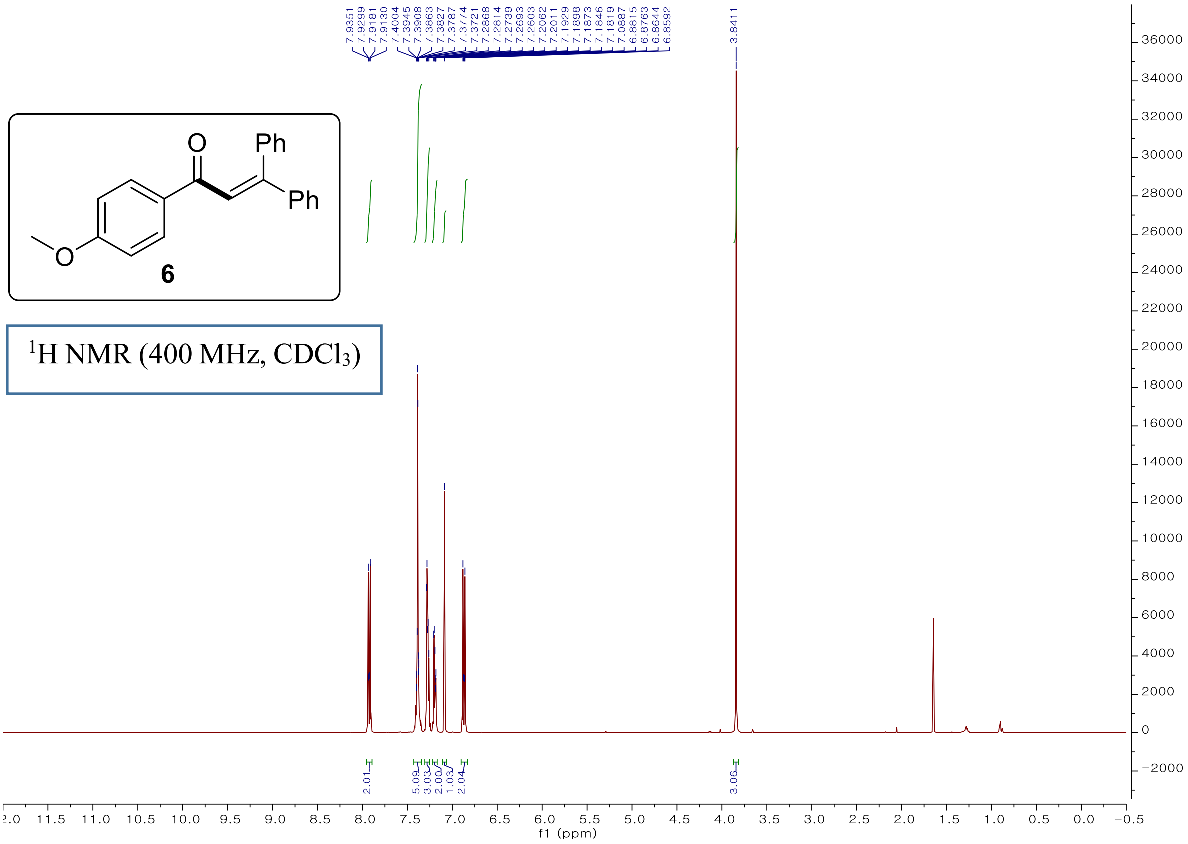
**4s**

$^{13}$C NMR (100 MHz, CDCl$_3$)



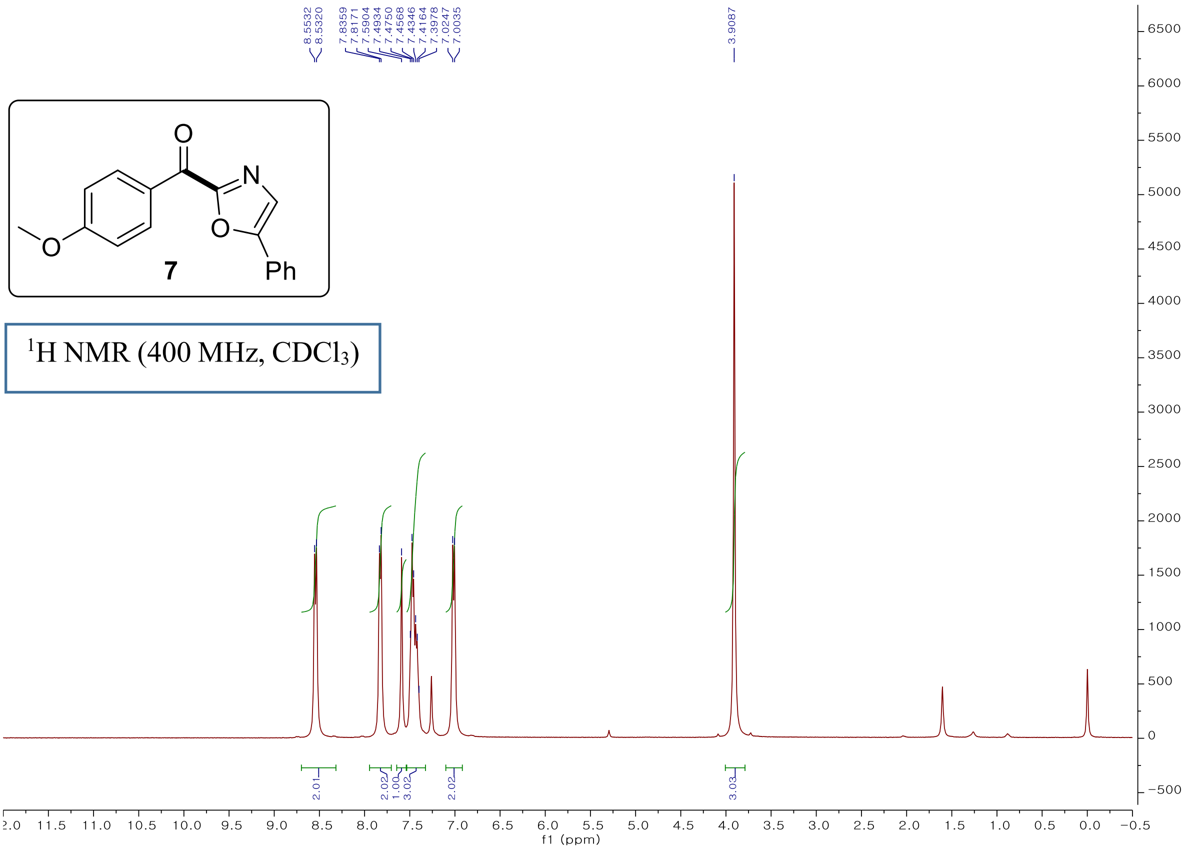
**5**

$^{1}$H NMR (500 MHz, CDCl$_3$)



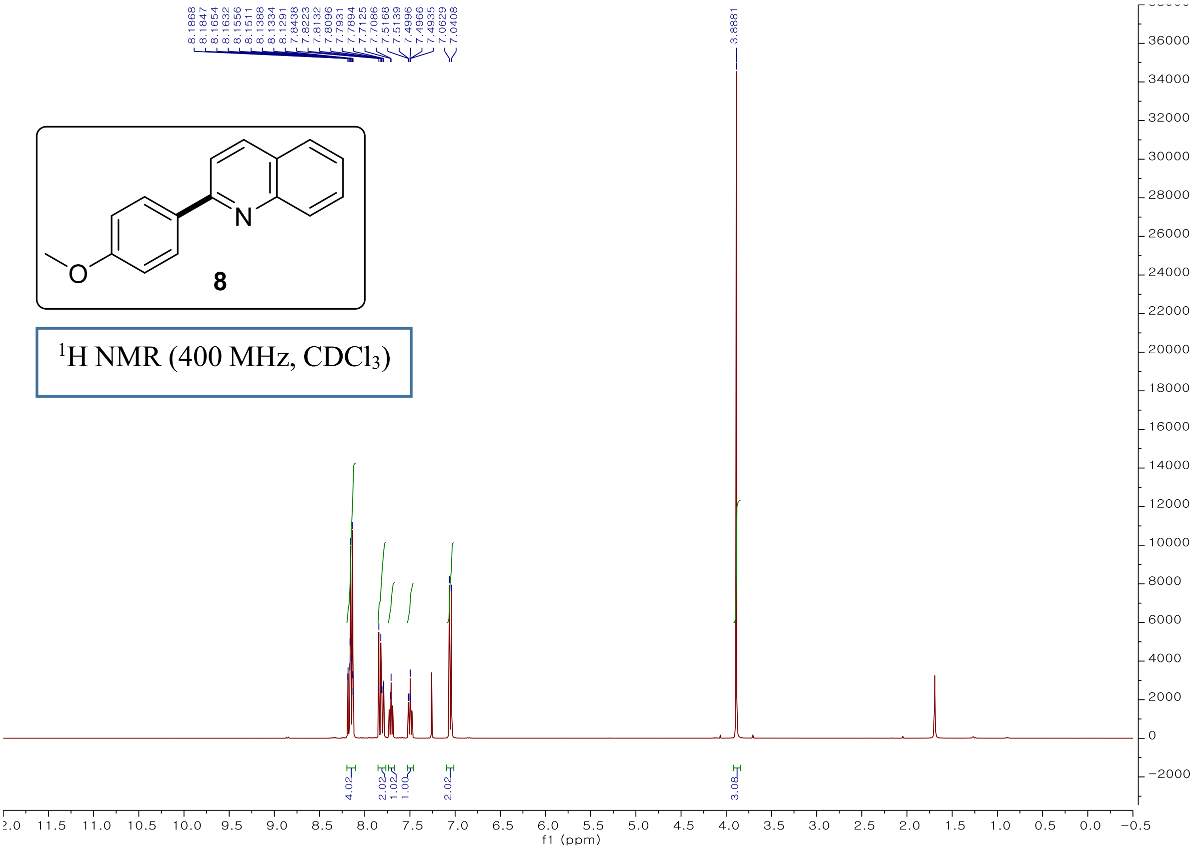
**6**

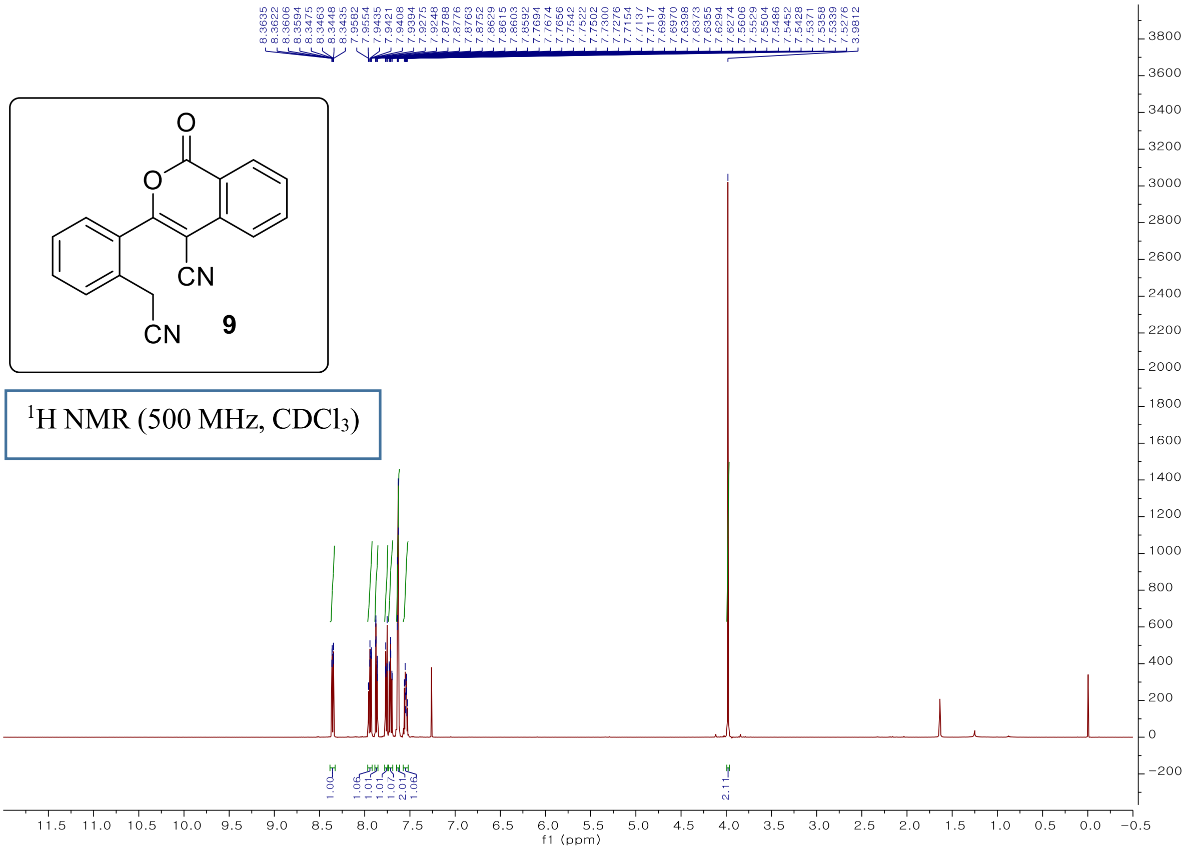
$^1$H NMR (400 MHz, $CDCl_3$)

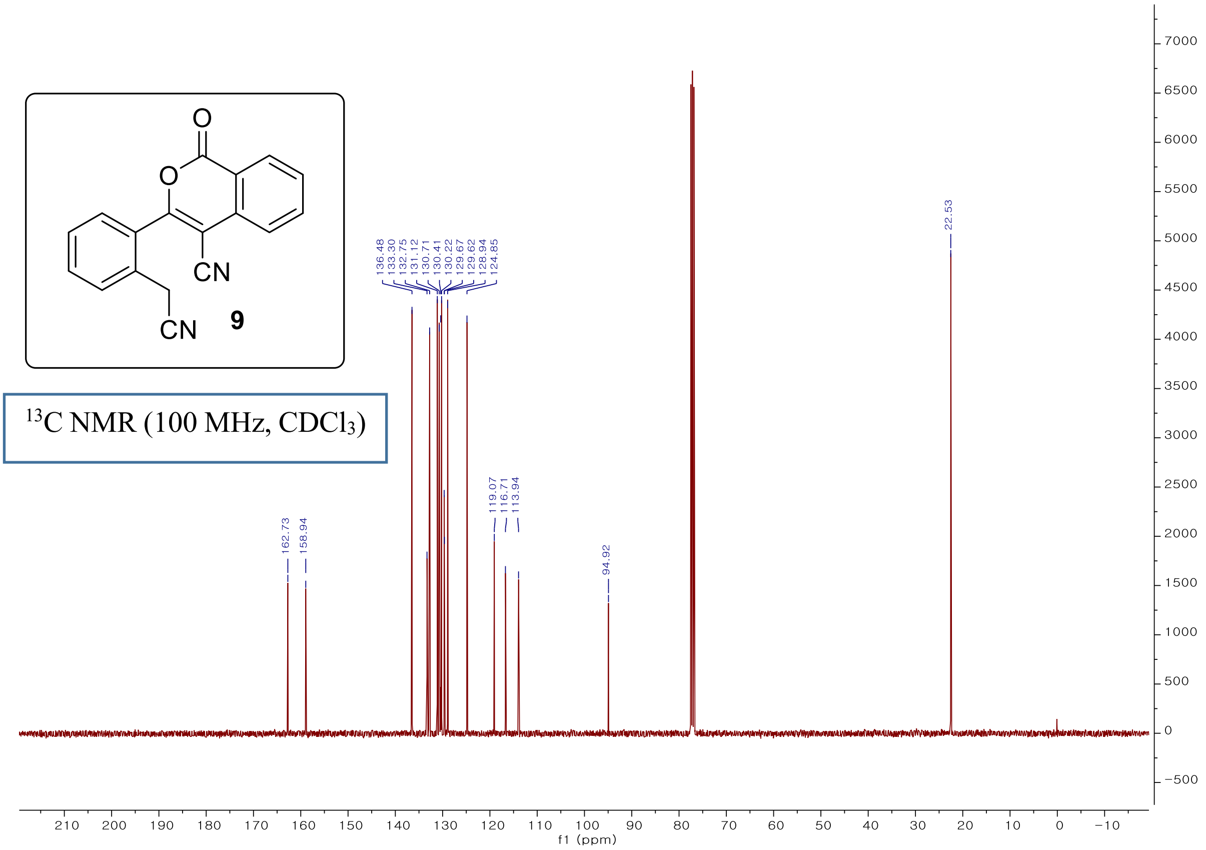


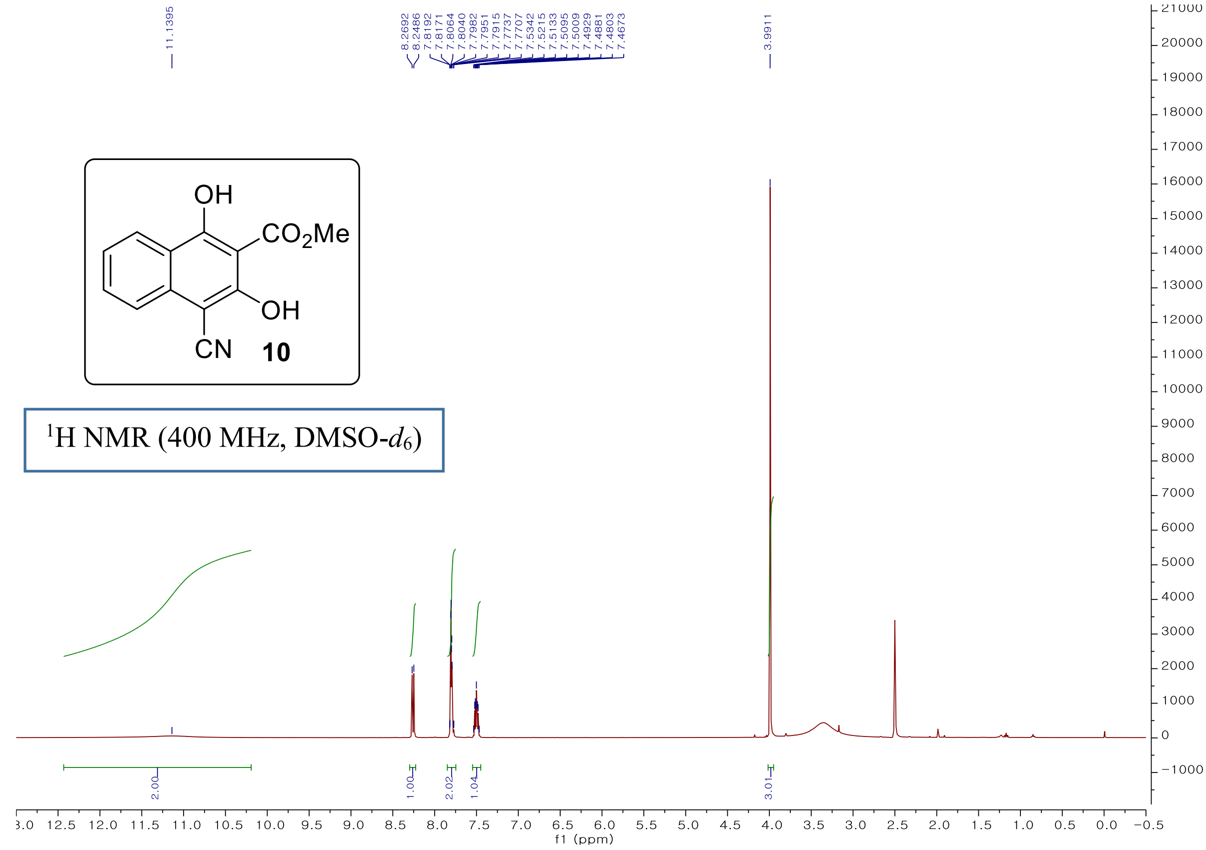
**7**

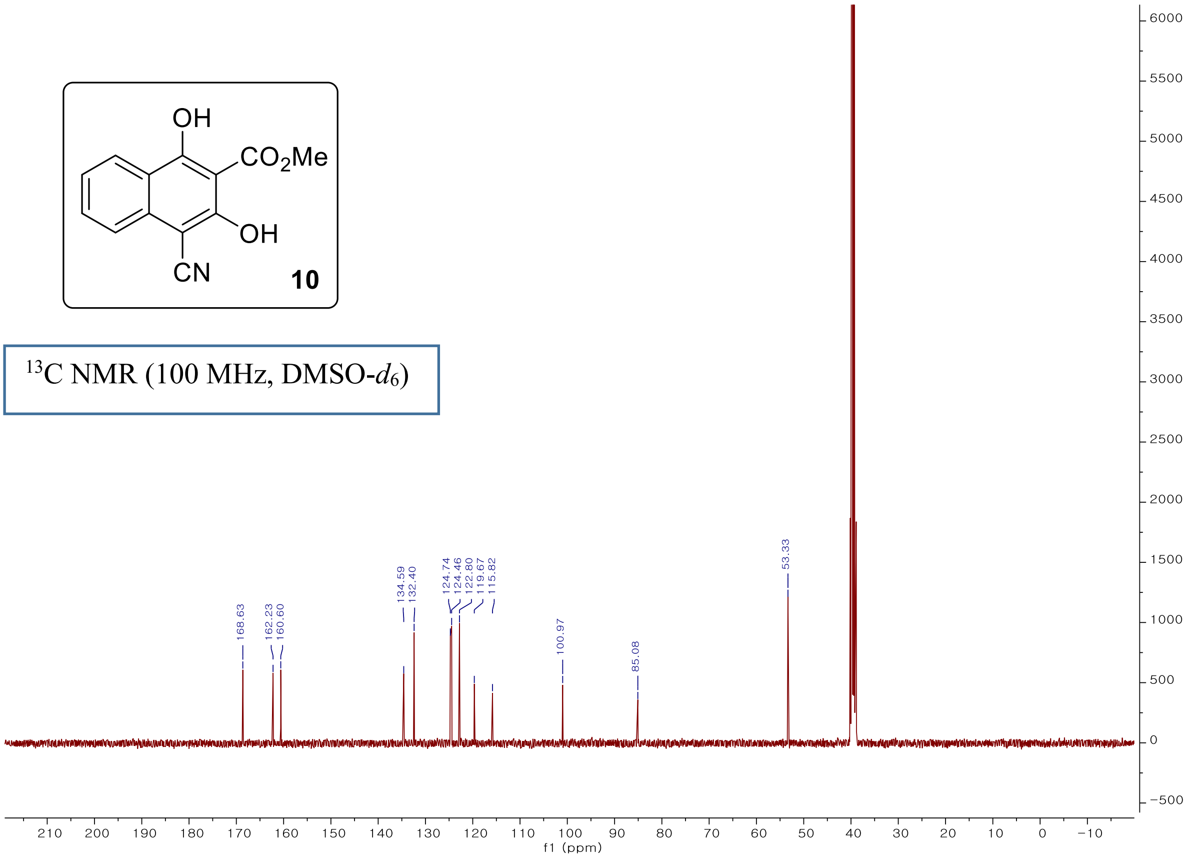
$^1$H NMR (400 MHz, $CDCl_3$)

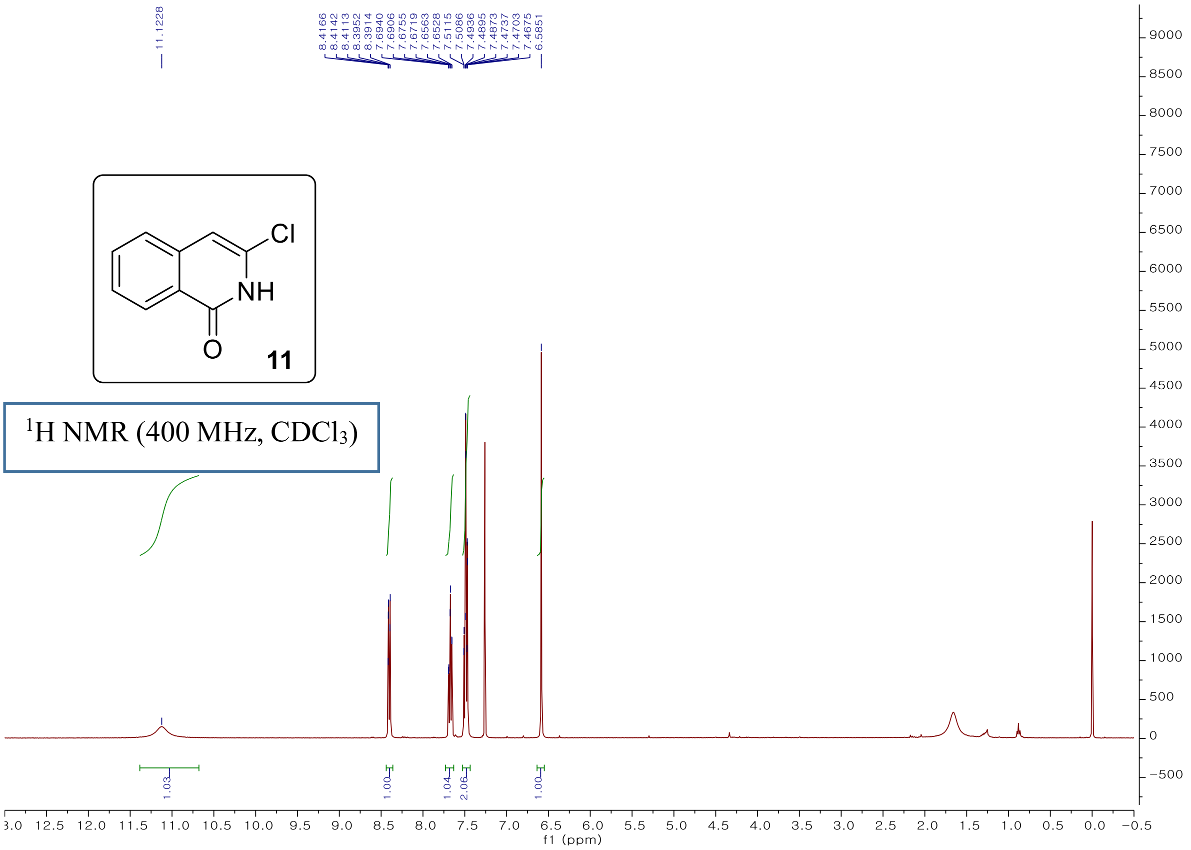

8.1868
8.1847
8.1654
8.1632
8.1556
8.1511
8.1388
8.1334
8.1291
7.8438
7.8223
7.8132
7.8096
7.7931
7.7894
7.7125
7.7086
7.5168
7.5139
7.4996
7.4966
7.4935
7.0629
7.0408
3.8881
N
O
8
$^1$H NMR (400 MHz, CDCl$_3$)
4.02
2.02
1.02
1.00
2.02
3.08
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

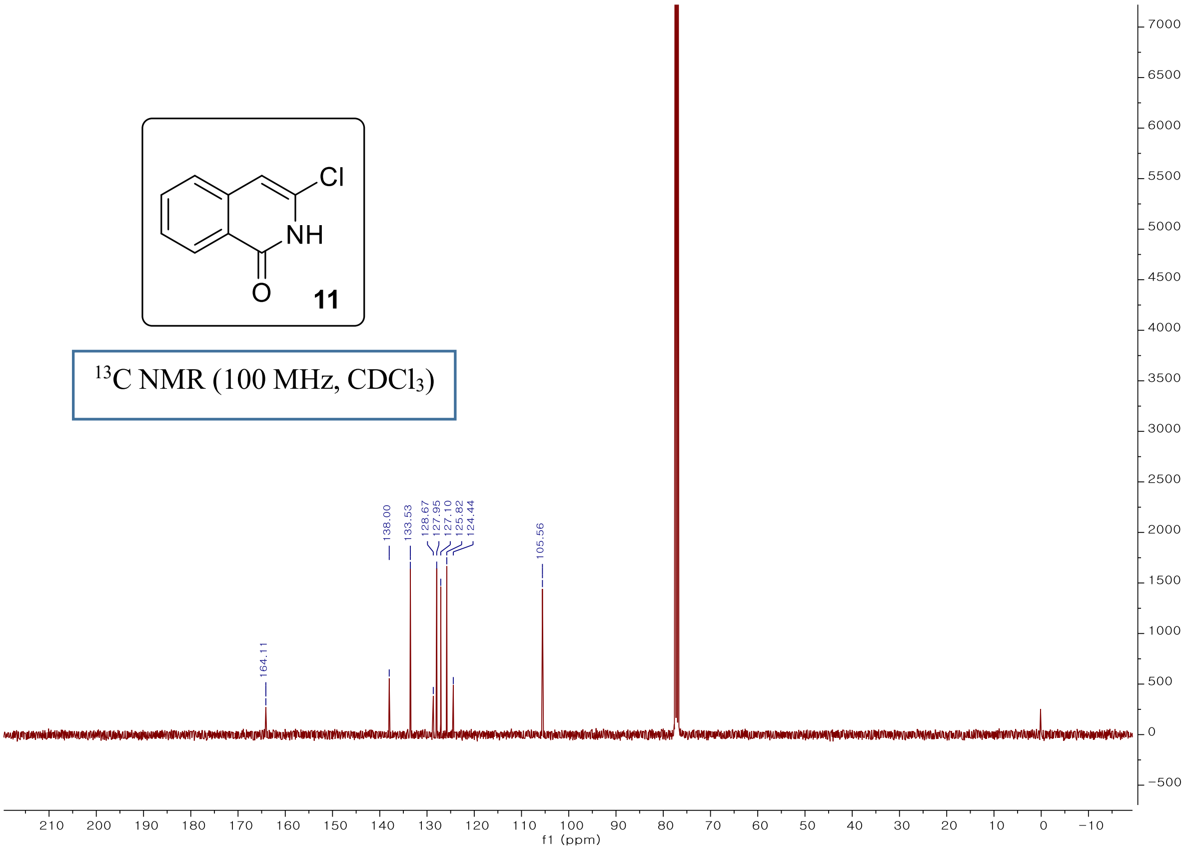

8.3635
8.3622
8.3606
8.3594
8.3475
8.3463
8.3448
8.3435
7.9582
7.9554
7.9435
7.9421
7.9408
7.9394
7.9275
7.9248
7.8788
7.8776
7.8763
7.8752
7.8629
7.8615
7.8603
7.8592
7.7694
7.7674
7.7656
7.7542
7.7522
7.7502
7.7300
7.7276
7.7154
7.7137
7.7117
7.6994
7.6970
7.6398
7.6373
7.6355
7.6294
7.6274
7.5606
7.5529
7.5504
7.5486
7.5452
7.5428
7.5371
7.5358
7.5339
7.5276
3.9812
O
O
CN
CN
9
$^1$H NMR (500 MHz, CDCl$_3$)
1.00
1.06
1.01
1.01
1.07
2.01
1.06
2.11
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


O
O
CN
CN
9
$^{13}$C NMR (100 MHz, CDCl$_3$)
136.48
133.30
132.75
131.12
130.71
130.41
130.22
129.67
129.62
128.94
124.85
162.73
158.94
119.07
116.71
113.94
94.92
22.53
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


OH
CO$_2$Me
OH
CN
10
$^1$H NMR (400 MHz, DMSO-$d_6$)
11.1395
8.2692
8.2486
7.8192
7.8171
7.8064
7.8040
7.7982
7.7951
7.7915
7.7737
7.7707
7.5342
7.5215
7.5133
7.5095
7.5009
7.4929
7.4881
7.4803
7.4673
3.9911
2.00
1.00
2.02
1.04
3.01
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


OH
CO$_2$Me
OH
CN
10
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
168.63
162.23
160.60
134.59
132.40
124.74
124.46
122.80
119.67
115.82
100.97
85.08
53.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500


Cl
NH
O
11
$^1$H NMR (400 MHz, CDCl$_3$)
11.1228
8.4166
8.4142
8.4113
8.3952
8.3914
7.6940
7.6906
7.6755
7.6719
7.6563
7.6528
7.5115
7.5086
7.4936
7.4895
7.4873
7.4737
7.4703
7.4675
6.5851
1.03
1.00
1.04
2.06
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
9000 8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500



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$^{13}$C NMR (100 MHz, CDCl$_3$)