Electronic Supplementary Information

Synthesis of 2-arylethenesulfonyl fluorides and isoindolinones: Ru-catalyzed C-H activation of nitrones with ethenesulfonyl fluoride

Tong-Tong Wang,[a] and Li-Ming Zhao*[ab]

[a]*School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, Jiangsu, China*

[b]*State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, China*

*Email: lmzhao@jsnu.edu.cn

Table of Contents

General Methods. Solvents and reagents were used as purchased without further purification. The reaction progress was monitored by thin-layer chromatography (TLC) on silica gel plates. Visualization of the developed plates was performed under a UV lamp. Chromatographic purification was performed with silica gel (100-200 mesh size). Melting points were uncorrected. Nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on Bruker DPX 400 MHz and 100 MHz spectrometers in $CDCl_3$ or DMSO-d_6 with the chemical shift (δ) given in parts per million (ppm). Multiplicities were indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets) and so forth; the coupling constant (*J*) was given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Q-Exactive Focus Orbitrap mass spectrometer. Arylnitrones **1** were prepared according to the literature procedure. [1]

General Procedure for the Synthesis of Compound 3. Arylnitrones **1** (0.2 mmol, 1.0 equiv), ethenesulfonyl fluoride **2** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (0.02 mmol, 0.1 equiv), $AgSbF_6$ (0.06 mmol, 0.3 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 2.0 equiv), 1,4-benzoquinone (0.4 mmol, 2.0 equiv), and 1,2-dichloroethane (2.0 mL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to provide compound **3**.

*(E)-2-(2-(Tert-butylcarbamoyl)phenyl)ethene-1-sulfonyl fluoride (**3a**)*. White solid (45 mg, 79% yield), ethyl acetate/petroleum ether = 1:5. mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 15.6 Hz, 1H), 7.60-7.58 (m, 1H), 7.51-7.49 (m, 3H), 6.86 (dd, *J* = 15.6, 1.6Hz,

1H), 5.70 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 146.8 (d, *J* = 3.2 Hz), 139.1, 132.1, 130.5, 129.3 (d, *J* = 1.4 Hz), 128.1, 127.7, 120.0 (d, *J* = 27.9 Hz), 52.7, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}FNO_3S$ 286.0908; found 286.0900.

*(E)-2-(2-(Tert-butylcarbamoyl)-5-methoxyphenyl)ethene-1-sulfonyl fluoride (**3b**)*. Yellow solid (55 mg, 87% yield), ethyl acetate/petroleum ether = 1:5. mp 122-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 15.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 5.77 (s, 1H), 3.86 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 160.9, 147.2 (d, *J* = 4.1 Hz), 131.5, 131.2, 129.5, 120.0 (d, *J* = 28.1 Hz), 117.1, 113.1, 55.7, 52.4, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}FNO_4S$ 316.1013; found 316.1018.

*(E)-2-(2-(Tert-butylcarbamoyl)-5-(methylthio)phenyl)ethene-1-sulfonyl fluoride (**3c**)*. Yellow solid (52 mg, 78% yield), ethyl acetate/petroleum ether = 1:10. mp 116-118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 15.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.83 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.71 (s, 1H), 2.53 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 146.7 (d, *J* = 3.2 Hz), 142.7, 135.0, 130.1 (d, *J* = 1.4 Hz), 128.6, 128.1, 124.8, 120.4 (d, *J* = 28.1 Hz), 52.6, 28.8, 15.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}FNO_3S_2$ 332.0785; found 332.0791.

*(E)-2-(4-(Tert-butylcarbamoyl)-[1,1'-biphenyl]-3-yl)ethene-1-sulfonyl fluoride (**3d**).* Yellow solid (66 mg, 91% yield), ethyl acetate/petroleum ether = 1:10. mp 122-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 15.6 Hz, 1H), 7.75 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 3H), 7.51-7.47 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 15.6 Hz, 1H), 5.72 (s, 1H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 146.9 (d, *J* = 3.9 Hz), 143.7, 139.0, 137.5, 130.5,

130.0, 129.2, 128.6, 128.3, 127.2, 126.8, 120.4 (d, J = 27.9 Hz), 52.7, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}FNO_3S$ 362.1221; found 362.1223.

*(E)-2-(2-(Tert-butylcarbamoyl)-5-fluorophenyl)ethene-1-sulfonyl fluoride (**3e**)*. Yellow solid (40 mg, 66% yield), ethyl acetate/petroleum ether = 1:10. mp 101-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 15.6 Hz, 1H), 7.53 (dd, J = 8.4, 5.6 Hz, 1H), 7.29-7.26 (m, 1H), 7.21 (td, J = 8.0, 2.0 Hz, 1H), 6.85 (dd, J = 15.6, 1.6 Hz, 1H), 5.67 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.2 (d, J = 250.8 Hz), 145.5, 135.3 (d, J = 3.5 Hz), 131.9 (d, J = 7.7 Hz), 130.0 (d, J = 8.5 Hz), 121.4 (d, J = 28.6 Hz), 118.9 (d, J = 21.4 Hz), 114.8 (d, J = 22.7 Hz), 52.8, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}F_2NO_3S$ 304.0813; found 304.0815.

*(E)-2-(2-(Tert-butylcarbamoyl)-5-chlorophenyl)ethene-1-sulfonyl fluoride (**3f**)*. White solid (48 mg, 75% yield), ethyl acetate/petroleum ether = 1:10. mp 115-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 15.6 Hz, 1H), 7.55 (s, 1H), 7.50-7.44 (m, 2H), 6.87 (dd, J = 15.6, 1.6 Hz, 1H), 5.73 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 145.3 (d, J = 3.1 Hz), 140.4, 138.2, 130.6, 129.3, 128.0, 127.6 (d, J = 1.4 Hz), 120.5 (d, J = 28.5 Hz, 1H), 52.9, 28.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}ClFNO_3S$ 320.0518; found 320.0512.

*(E)-2-(5-Bromo-2-(tert-butylcarbamoyl)phenyl)ethene-1-sulfonyl fluoride (**3g**).* White solid (40 mg, 55% yield), ethyl acetate/petroleum ether = 1:10. mp 85-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 15.2 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.60 (s, 1H), 7.44 (d, J = 8.8 Hz, 1H), 6.86 (dd, J = 15.2, 1.6 Hz, 1H), 5.83 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 145.3 (d, J = 2.8 Hz), 140.4, 133.5, 130.8, 129.3, 128.0, 126.4, 120.5 (d, J = 28.4 Hz), 52.9, 28.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}BrFNO_3S$ 364.0013; found 364.0014.

*Methyl (E)-4-(tert-butylcarbamoyl)-3-(2-(fluorosulfonyl)vinyl)benzoate (**3h**)*. Yellow solid

(50 mg, 73% yield), ethyl acetate/petroleum ether = 1:10. mp 187-188 ℃. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.23 (s, 1H), 8.15 (d, *J* = 16.0 Hz, 1H), 8.14 (d, *J* = 5.2 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 15.6 Hz, 1H), 5.77 (s, 1H), 3.97 (s, 3H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.3, 145.5 (d, *J* = 3.4 Hz), 142.5, 132.7, 132.1, 129.6, 129.1, 128.0, 121.5 (d, *J* = 27.9 Hz), 53.0, 52.9, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}FNO_5S$ 344.0962; found 344.0962.

*(E)-2-(2-(Tert-butylcarbamoyl)-5-hydroxyphenyl)ethene-1-sulfonyl fluoride (**3i**)*. White solid (46 mg, 76% yield), ethyl acetate/petroleum ether = 1:3. mp 105-106 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (s, 1H), 8.15 (d, *J* = 15.2 Hz, 1H), 8.00 (s, 1H), 7.79 (d, *J* = 15.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.25 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.3, 158.5, 147.4 (d, *J* = 2.8 Hz), 131.1, 130.5, 130.1, 119.2 (d, *J* = 25.3 Hz), 118.8, 113.9, 51.1, 28.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}FNO_4S$ 302.0857; found 302.0858.

*(E)-2-(2-(Tert-butylcarbamoyl)-6-methylphenyl)ethene-1-sulfonyl fluoride (**3j**)*. Yellow solid (40 mg, 67% yield), ethyl acetate/petroleum ether = 1:5. mp 121-122 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.30-7.27 (m, 2H), 6.81 (dd, *J* = 15.6, 2.0 Hz, 1H), 5.68 (s, 1H), 2.42 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 146.6 (d, *J* = 2.8 Hz), 143.2, 139.3, 131.2, 128.4, 128.0, 126.3, 118.9 (d, *J* = 27.9 Hz), 52.6, 28.8, 21.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}FNO_3S$ 300.1064; found 300.1066.

*(E)-2-(2-(Tert-butylcarbamoyl)-6-chlorophenyl)ethene-1-sulfonyl fluoride (**3k**)*. White solid (39 mg, 61% yield), ethyl acetate/petroleum ether = 1:10. mp 120-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 15.6 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.47-7.45 (m, 2H), 6.85 (dd, *J* =

15.2, 1.6 Hz, 1H), 5.77 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 145.3 (d, *J* = 2.8 Hz), 137.2, 136.7, 131.8, 131.2, 129.1, 127.9, 121.4 (d, *J* = 28.6 Hz), 52.8, 28.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}ClFNO_3S$ 320.0518; found 320.0518.

*(E)-2-(2-Bromo-6-(tert-butylcarbamoyl)phenyl)ethene-1-sulfonyl fluoride (**3l**).* White solid (39 mg, 54% yield), ethyl acetate/petroleum ether = 1:10. mp 99-101 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 15.2 Hz, 1H), 7.63-7.62 (m, 2H), 7.45 (d, *J* = 8.8 Hz, 1H), 6.86 (dd, *J* = 15.6 Hz, 1.2 Hz, 1H), 5.74 (s, 1H). 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 145.4 (d, *J* = 2.8 Hz), 140.5, 133.6, 130.9, 129.4, 128.1, 126.5, 120.6 (d, *J* = 28.5 Hz), 53.0, 28.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}BrFNO_3S$ 364.0013; found 364.0014.

*(E)-2-(2-(Tert-butylcarbamoyl)-3-methylphenyl)ethene-1-sulfonyl fluoride (**3m**)*. White solid (41 mg, 68% yield), ethyl acetate/petroleum ether = 1:10. mp 168-170 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 15.2 Hz, 1H), 7.41-7.39 (m, 1H), 7.36-7.33 (m, 2H), 6.89 (dd, *J* = 15.6, 2.0 Hz, 1H), 5.62 (s, 1H), 2.38 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 146.3 (d, *J* = 3.0 Hz), 139.6, 135.9, 134.2, 129.3, 127.8 (d, *J* = 1.4 Hz), 124.9, 120.0 (d, *J* = 28.0 Hz), 52.7, 28.7, 18.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}FNO_3S$ 300.1064; found 300.1065.

*(E)-2-(2-(Tert-butylcarbamoyl)-3-chlorophenyl)ethene-1-sulfonyl fluoride (**3n**)*. White solid (25 mg, 39% yield), ethyl acetate/petroleum ether = 1:5. mp 177-179 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 15.6, 2.0 Hz, 1H), 5.66 (s, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 144.9 (d, *J* = 3.2 Hz), 138.4, 133.0, 132.2, 130.4, 130.2 (d, *J* = 1.5 Hz), 126.1, 121.8 (d, *J* = 28.7 Hz), 53.1, 28.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}ClFNO_3S$

320.0518; found 320.0519.

*(E)-2-(2-(Tert-butylcarbamoyl)-4,5-dimethoxyphenyl)ethene-1-sulfonyl fluoride (**3o**)*. Yellow solid (57 mg, 83% yield), ethyl acetate/petroleum ether = 1:10. mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.6 Hz, 1H), 6.97 (s, 2H), 6.75 (dd, *J* = 15.2, 1.6 Hz, 1H), 5.64 (s, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, CDCl3) δ 167.0, 152.4, 150.4, 146.2 (d, *J* = 3.3 Hz), 134.1, 121.4, 117.4 (d, *J* = 27.8 Hz), 110.4, 109.1, 56.4, 56.3, 52.8, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{21}FNO_5S$ 346.1119; found 346.1120.

*(E)-2-(2-(Tert-butylcarbamoyl)-4,5-dichlorophenyl)ethene-1-sulfonyl fluoride (**3p**)*. Yellow solid (36 mg, 51% yield), ethyl acetate/petroleum ether = 1:10. 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 15.6 Hz, 1H), 7.67 (s, 1H), 7.59 (s, 1H), 6.87 (d, *J* = 15.6 Hz, 1H), 5.70 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 144.1 (d, *J* = 3.3 Hz), 138.0, 136.2, 135.0, 129.6, 129.1 (d, *J* = 1.5 Hz), 121.6 (d, *J* = 29.0 Hz), 53.0, 28.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}Cl_2FNO_3S$ 354.0128; found 354.0131.

*(E)-2-(3-(Tert-butylcarbamoyl)naphthalen-2-yl)ethene-1-sulfonyl fluoride (**3q**).* White solid (55 mg, 82% yield), ethyl acetate/petroleum ether = 1:10. mp 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 15.2 Hz, 1H), 8.00 (s, 1H), 7.92 (s, 1H), 7.88-7.86 (m, 2H), 7.64-7.61 (m, 2H), 6.93 (dd, *J* = 15.6, 2.0 Hz, 1H), 5.93 (s, 1H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 147.4 (d, *J* = 3.2 Hz), 135.1, 133.8, 133.1, 129.7, 129.1, 128.7, 128.4, 128.2, 127.6, 126.9 (d, *J* = 1.5 Hz), 119.6 (d, *J* = 27.8 Hz), 52.6, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{19}FNO_3S$ 336.1064; found 336.1064.

*(E)-2-(2-(Benzylcarbamoyl)phenyl)ethene-1-sulfonyl fluoride (**3s**)*. White solid (29 mg, 45% yield), ethyl acetate/petroleum ether = 1:5. mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33

(d, J = 15.6 Hz, 1H), 7.63-7.61 (m, 1H), 7.57-7.52 (m, 3H), 7.40-7.32 (m, 5H), 6.83 (d, J = 15.6 Hz, 1H), 6.25 (s, 1H), 4.64 (d, J = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 146.8 (d, J = 2.8 Hz), 137.5, 137.3, 132.0, 131.1, 130.1, 129.1, 128.2, 128.1, 128.1, 127.8, 120.3 (d, J = 28.2 Hz), 44.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}FNO_3S$ 320.0751; found 320.0752.

General Procedure for the Synthesis of Compound 5. Arylnitrones **4** (0.2 mmol, 1.0 equiv), ethenesulfonyl fluoride **2** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (0.02 mmol, 0.1 equiv), $AgSbF_6$ (0.06 mmol, 0.3 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.4 mmol, 2.0 equiv), 1,4-benzoquinone (0.4 mmol, 2.0 equiv), and trifluoroethanol (2.0 mL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 120 °C on a heating block for 6 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to provide compound **5**.

*(2-Methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5a**)*. Yellow solid (28 mg, 58% yield), ethyl acetate/petroleum ether = 1:10. mp 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 1H), 7.64-7.63 (m, 2H), 7.59-7.54 (m, 1H), 4.96 (t, J = 5.2 Hz, 1H), 3.94 (dt, J = 15.2, 3.6 Hz, 1H), 3.86 (dt, J = 15.2, 4.8 Hz, 1H), 3.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 141.7, 132.5, 131.7, 129.8, 124.2, 122.7 (d, J = 1.5 Hz), 57.1, 53.2 (d, J = 15.7 Hz), 28.1 (d, J = 1.3 Hz). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}FNO_3S$ 244.0438; found 244.0433.

*(6-Methoxy-2-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5b**)*. Yellow solid (39 mg, 71% yield), ethyl acetate/petroleum ether = 1:5. mp 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 1H), 7.10 (s, 1H), 7.05 (dd, J = 8.4, 2.0 Hz, 1H), 4.89 (t, J = 5.2

Hz, 1H), 3.91 (dt, *J* = 14.8, 3.2 Hz, 1H), 3.89 (s, 3H), 3.81 (dt, *J* = 15.2, 4.8 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.5, 144.1, 125.6, 124.1, 116.0, 107.8 (d, *J* = 1.5 Hz), 56.8, 55.9, 53.4 (d, *J* = 15.6 Hz), 28.1 (d, *J* = 1.0 Hz). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}FNO_4S$ 274.0544; found 274.0552.

*(2-Methyl-6-(methylthio)-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5c**)*. Yellow solid (36 mg, 62% yield), ethyl acetate/petroleum ether = 1:5. mp 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 4.91 (t, *J* = 4.8 Hz, 1H), 3.93 (dt, *J* = 15.2, 2.8 Hz, 1H), 3.83 (dt, *J* = 15.2, 4.4 Hz, 1H), 3.19 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 145.6, 142.7, 128.1, 126.8, 124.2, 119.2 (d, *J* = 1.6 Hz), 56.8, 53.1 (d, *J* = 15.7 Hz), 28.1 (d, *J* = 1.0 Hz), 15.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}FNO_3S_2$ 290.0315; found 290.0327.

*(6-Fluoro-2-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5d**)*. White solid (25 mg, 49% yield), ethyl acetate/petroleum ether = 1:5. mp 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.28-7.24 (m, 1H), 4.94 (t, *J* = 4.8 Hz, 1H), 3.95 (dt, *J* = 15.2, 3.6 Hz, 1H), 3.83 (dq, *J* = 15.2, 4.0 Hz, 1H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 165.5 (d, *J* = 252.3 Hz), 144.0 (d, *J* = 10.2 Hz), 127.8 (d, *J* = 2.6 Hz), 126.3 (d, *J* = 9.8 Hz), 117.6 (d, *J* = 23.2 Hz), 110.6 (d, *J* = 26.9 Hz), 56.7 (d, *J* = 3.1 Hz), 52.7 (d, *J* = 16.2 Hz), 28.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}F_2NO_3S$ 262.0344; found 262.0346.

*(5-Methoxy-2-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5e**)*. Yellow solid (25 mg, 46% yield), ethyl acetate/petroleum ether = 1:5. mp 203-205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.16 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.90

(t, J = 4.8 Hz, 1H), 3.91 (dt, J = 15.2, 3.6 Hz, 1H), 3.88 (s, 3H), 3.80 (dt, J = 15.2, 4.0 Hz, 1H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 161.1, 133.5, 133.2, 123.6 (d, J = 1.6 Hz), 120.4, 107.0, 56.6, 55.6, 53.1 (d, J = 15.2 Hz), 28.1 (d, J = 1.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}FNO_4S$ 274.0544; found 274.0546.

*(5-Chloro-2-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5f**)*. White solid (20 mg, 36% yield), ethyl acetate/petroleum ether = 1:5. mp 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.61-7.57 (m, 2H), 4.94 (t, J = 5.6 Hz, 1H), 3.96 (dt, J = 15.2, 3.6 Hz, 1H), 3.82 (dq, J = 15.6, 3.6 Hz, 1H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 139.7, 136.3, 133.6, 132.6, 124.4, 124.1 (d, J = 1.5 Hz), 56.8, 52.6 (d, J = 16.0 Hz), 28.1 (d, J = 1.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}ClFNO_3S$ 278.0048; found 278.0050.

*(2,4-Dimethyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**5g**)*. Yellow solid (16 mg, 31% yield), ethyl acetate/petroleum ether = 1:5. mp 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 4.90 (t, J = 4.8 Hz, 1H), 3.91-3.81 (m, 2H), 3.19 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 142.3, 138.4, 131.9, 131.7, 128.7, 119.9 (d, J = 1.4 Hz), 56.5, 53.6 (d, J = 15.3 Hz), 28.0 (d, J = 1.4 Hz), 17.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}FNO_3S$ 258.0595; found 258.0595.

*(2-Methyl-3-oxo-2,3-dihydro-1H-benzo[f]isoindol-1-yl)methanesulfonyl fluoride (**5h**)*. Yellow solid (36 mg, 61% yield), ethyl acetate/petroleum ether = 1:5. mp 198-200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.07 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.66-7.59 (m, 2H), 5.13 (t, J = 5.2 Hz, 1H), 4.00 (dt, J = 15.6, 3.6 Hz, 1H), 3.92 (dt, J = 15.2, 4.4 Hz, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 136.7, 135.2, 133.4, 129.7, 128.7, 128.5, 128.4, 127.3, 124.7, 122.2, 56.9, 53.8 (d, J = 15.2 Hz), 28.3. HRMS (ESI)

m/z: $[M + H]^+$ calcd for $C_{14}H_{13}FNO_3S$ 294.0595; found 294.0597.

Scale Synthesis of 1.0 mmol 3a. *N-Tert*-butyl-*α*-phenylnitrone **1a** (177 mg, 1.0 mmol), ethenesulfonyl fluoride **2** (166 μL, 2.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (61.2 mg, 0.1 mmol), $AgSbF_6$ (103 mg, 0.3 mmol), $Cu(OAc)_2 \cdot H_2O$ (363 mg, 2.0 mmol), 1,4-benzoquinone (216 mg, 2.0 mmol), and 1,2-dichloroethane (10 mL) were placed in a 38 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford **3a** as a white solid (199 mg, 70% yield).

Procedure for the Synthesis of Compound 6. *N-Tert*-butyl-*α*-phenylnitrone **1a** (35.4 mg, 0.2 mmol), ethenesulfonyl fluoride **2** (33 μL, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2 \cdot H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), and 1,2-dichloroethane (2.0 mL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. Then, 1,8-diazabicyclo[5.4.0]undec-7-ene (15 μL, 0.1 mmol) was added to the reaction mixture. The resulting mixture was stirred at 100 °C on a heating block for 14 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the compound **6**.

*(2-(Tert-butyl)-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**6**)*. Yellow solid (38 mg, 67% yield), ethyl acetate/petroleum ether = 1:5. mp 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H),

5.23 (d, J = 8.4 Hz, 1H), 4.18 (dt, J = 15.2, 1.2 Hz, 1H), 3.65 (ddd, J = 11.2, 8.4, 2.8 Hz, 1H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 142.7, 132.7, 132.3, 129.6, 123.8, 122.6 (d, J = 2.4 Hz), 56.1, 55.9 (d, J = 13.2 Hz), 55.0, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}FNO_3S$ 286.0908; found 286.0901.

Procedure for the Synthesis of Compound 7. Compound **1u** (38.6 mg, 0.2 mmol), ethenesulfonyl fluoride **2** (33 μL, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2 \cdot H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), and 1,2-dichloroethane (2.0 mL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 8 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the compound **7**.

N-(Tert-butyl)benzo[e][1,2]oxathiine-5-carboxamide 2,2-dioxide (7). White solid (22 mg, 40% yield), ethyl acetate/petroleum ether = 1:5. mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 10.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 10.4 Hz, 1H), 5.79 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 152.1, 137.5, 133.6, 131.9, 124.1, 122.9, 120.8, 117.4, 52.7, 28.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}NO_4S$ 282.0795; found 282.0794.

Procedure for the Synthesis of Compound 8. To a solution of compound **3a** (28.5 mg, 0.1 mmol) and *p*-xylene (280 μL, 2.3 mmol) in dichloromethane (1.0 mL) was added $AlCl_3$ (53 mg, 0.4 mmol) at -20 °C. The resulting mixture was allowed to reach room temperature and stirred for 4 h. After completion of the reaction, the mixture was quenched with saturated $NaHCO_3$

(10 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried, concentrated, and the residue was purified by flash chromatography on silica gel to afford the compound **8**.

*(E)-N-(Tert-butyl)-2-(2-((2,5-dimethylphenyl)sulfonyl)vinyl)benzamide (**8**)*. White solid (30 mg, 82% yield), ethyl acetate/petroleum ether = 1:5. mp 99-101 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 15.6 Hz, 1H), 7.89 (s, 1H), 7.51-7.39 (m, 4H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 15.6 Hz, 1H), 5.65 (s, 1H), 2.60 (s, 3H), 2.39 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 140.1, 138.9, 137.5, 136.7, 135.4, 134.5, 132.7, 130.7, 130.4, 130.1, 129.9, 129.3, 127.7, 127.6, 52.4, 28.7, 20.9, 20.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{26}NO_3S$ 372.1628; found 372.1632.

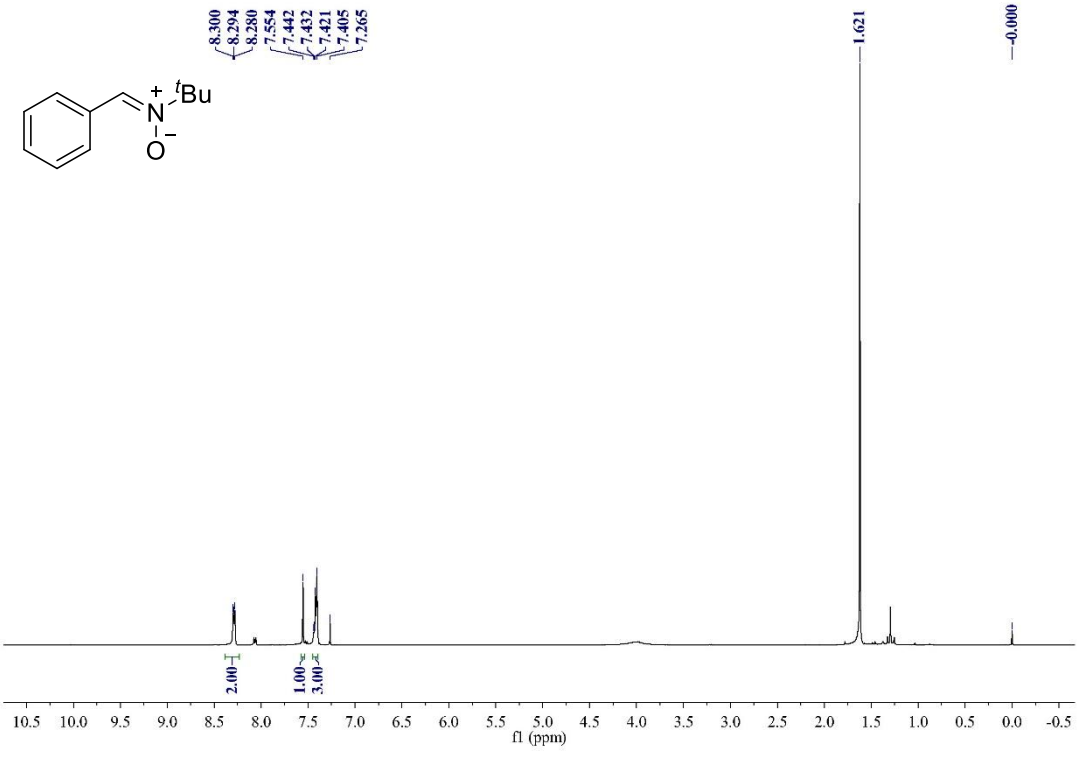
Mechanistic Studies

(a) Control experiment. *N-Tert*-butylbenzamide **9** (35.4 mg, 0.2 mmol), ethenesulfonyl fluoride **2** (33 μL, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2{\cdot}H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), and 1,2-dichloroethane (2.0 mL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the compound **3a** in ca. 10% yield.

(c) ^{18}O-Incorporation experiment. Compound **1a** (35.4 mg, 0.2 mmol), ethenesulfonyl fluoride **2** (33 μL, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2{\cdot}H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), 1,2-

dichloroethane (2.0 mL), and $H_2{}^{18}O$ (40 μL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the mixture products of compounds **3a** and **3a-^{18}O**.

(d) H/D exchange experiment with [RuCl$_2$(*p*-cymene)]$_2$. Compound **1a** (35.4 mg, 0.2 mmol), [RuCl$_2$(*p*-cymene)]$_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2{\cdot}H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), 1,2-dichloroethane (2.0 mL), and CD_3OD (80 μL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on



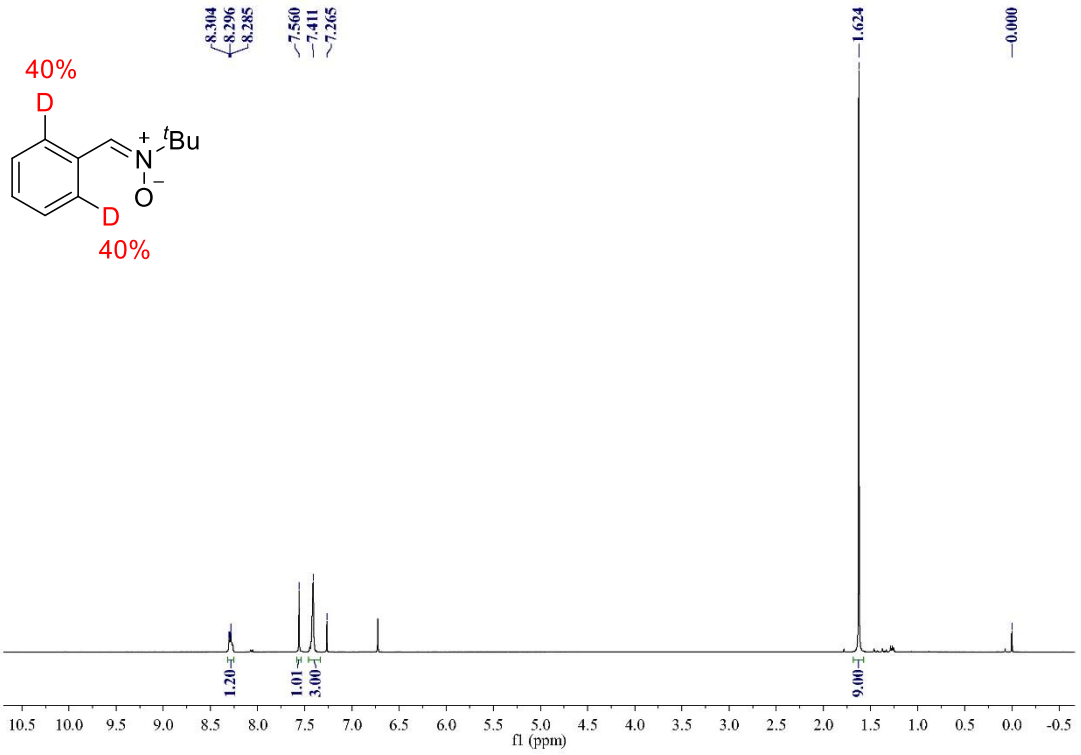


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a** and **1a-*d***

silica gel to recover the compound **1a** in 36% yield. And H/D exchange at the *ortho*-position (40% D) of **1a** was observed by ^{1}H NMR analysis (**Figure S1**).

(e) Deuterium-labelling experiment of 1a and 2. Compound **1a** (35.4 mg, 0.2 mmol), ethenesulfonyl fluoride **2** (33 μL, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2{\cdot}H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), 1,2-dichloroethane (2.0 mL), and CD_3OD (80 μL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the compound **3a-*d*** in 77% yield. And H/D exchanges at the α-position (42% D) of sulfonyl fluoride was observed by ^{1}H NMR analysis (**Figure S2**).

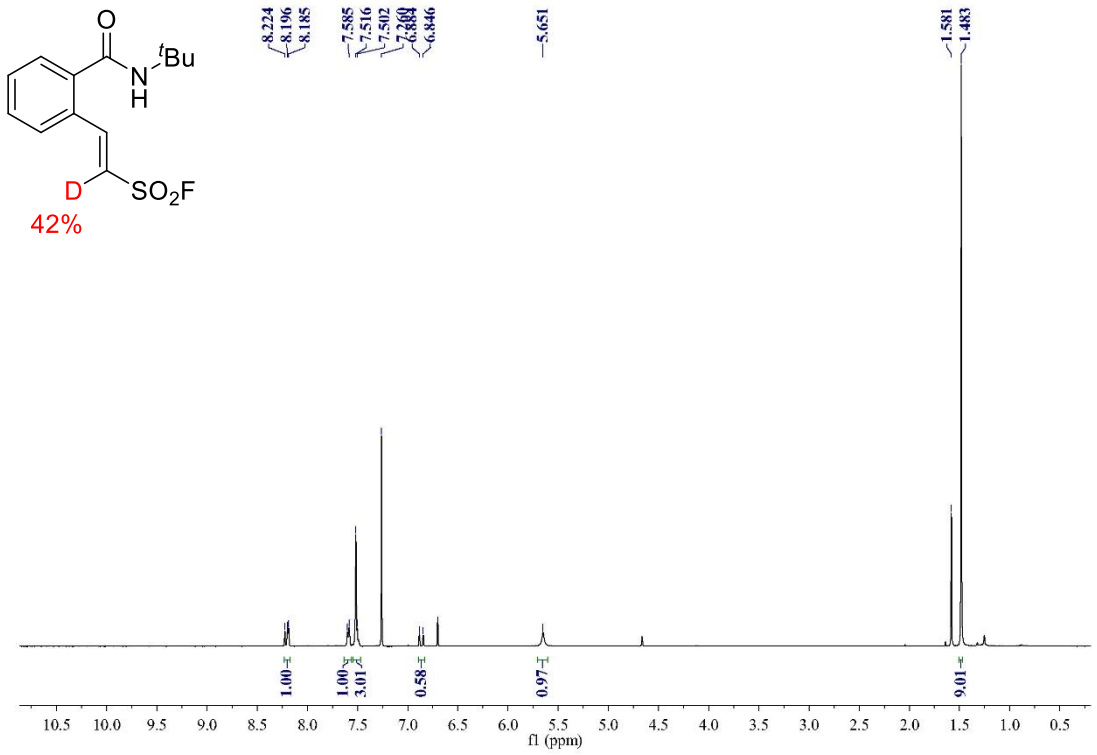
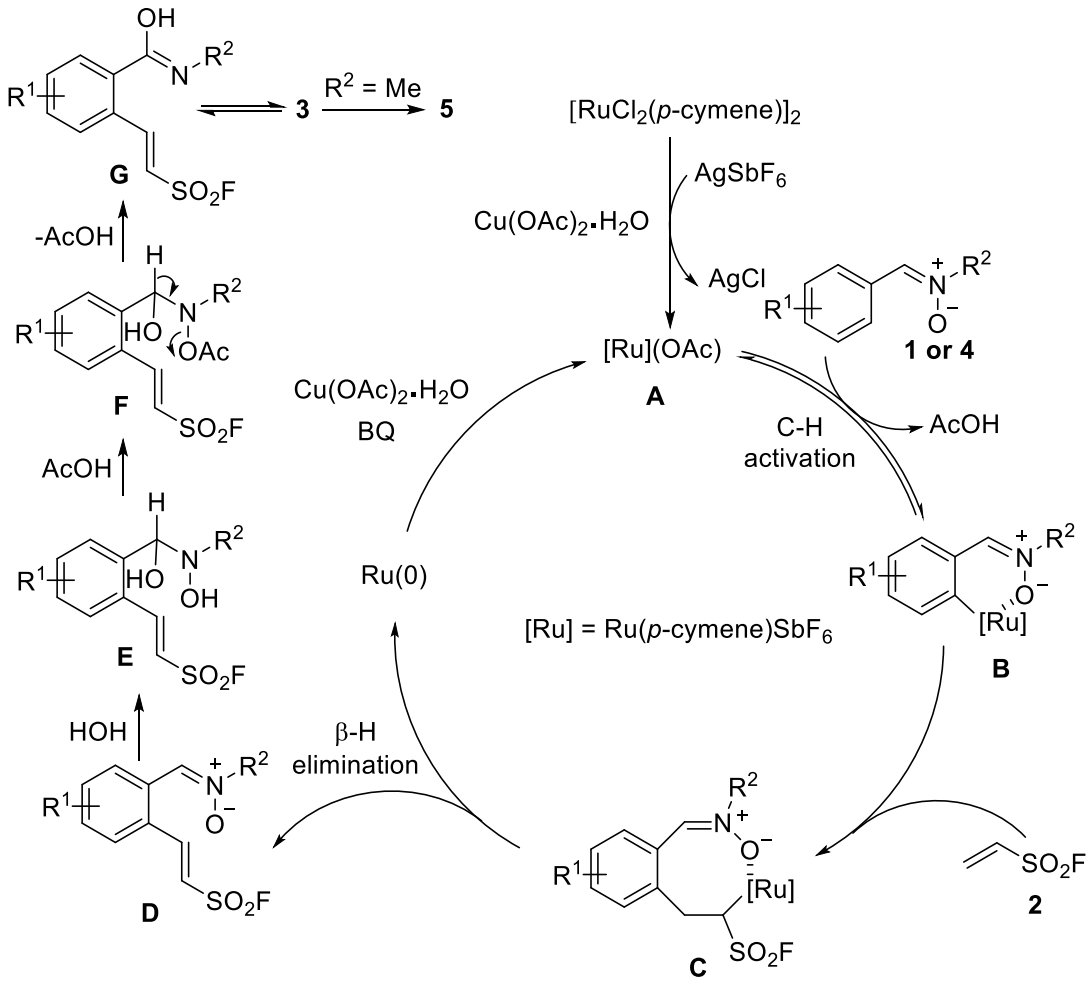
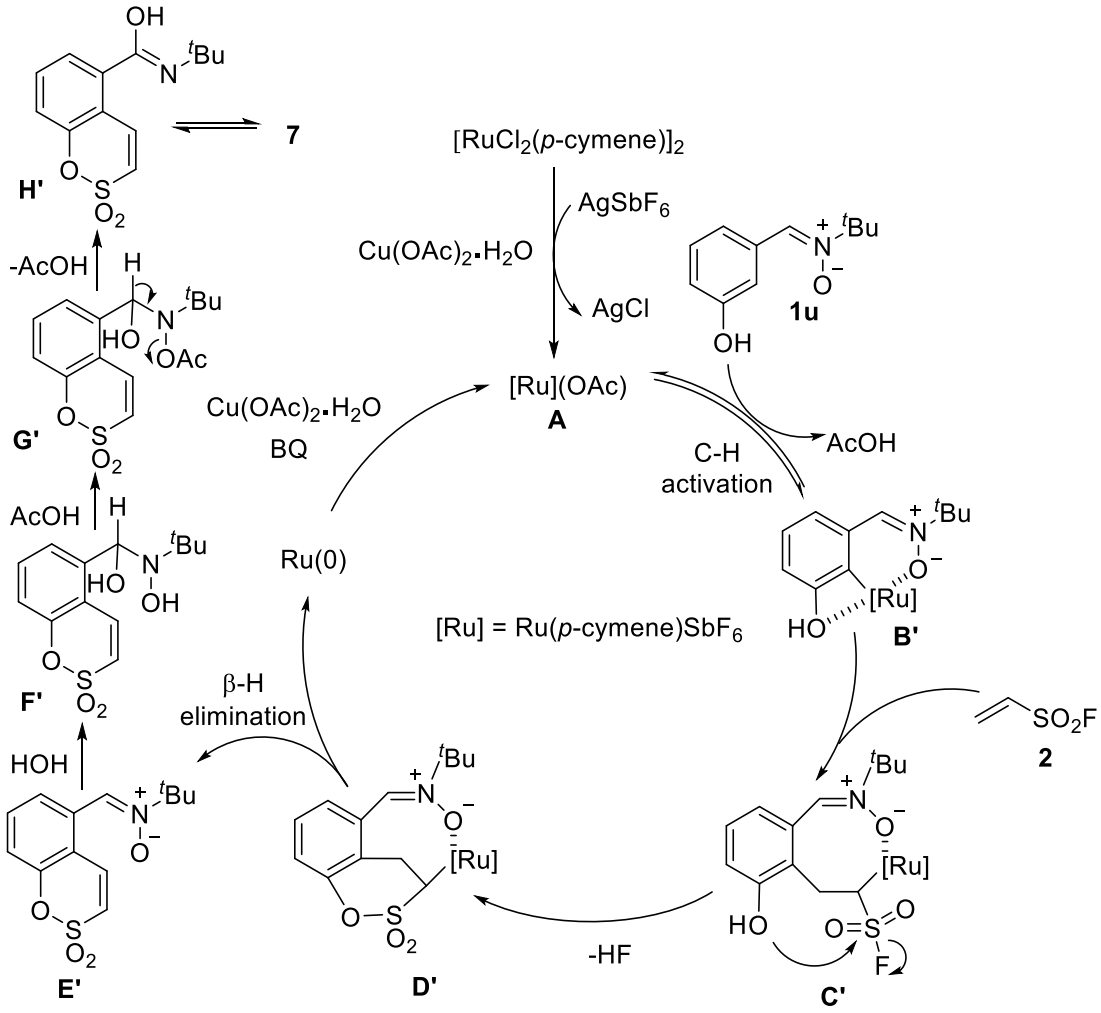


Figure S2 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a-*d***

(f) Intermolecular competition experiment between 1b and 1e. Compound **1b** (41.4 mg, 0.2 mmol), compound **1e** (39 mg, 0.2 mmol), ethenesulfonyl fluoride **2** (33 μL, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (20.6 mg, 0.06 mmol), $Cu(OAc)_2{\cdot}H_2O$ (72.6 mg, 0.4 mmol), 1,4-benzoquinone (43 mg, 0.4 mmol), and 1,2-dichloroethane (2.0 mL) were placed in a 15 mL pressure tube under the air atmosphere. The tube was then sealed and the reaction mixture was stirred at 100 °C on a heating block for 1 h. After completion of the reaction, the resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the compounds **3b** (26 mg, 0.412 mmol) and **3e** (3.0 mg, 0.049 mmol). The molar ratio of **3b** and **3e** was thus calculated as 8.5:1.

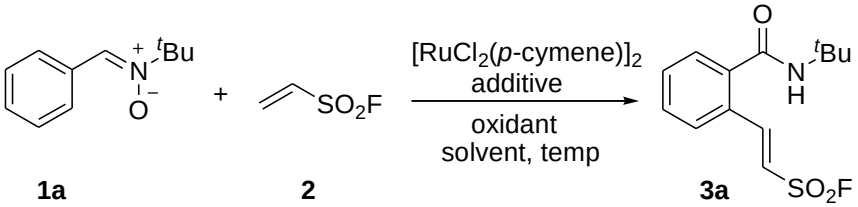


Scheme S1. Proposed Reaction Mechanism



Scheme S2. Proposed Reaction Mechanism for the Formation of 7

Table S1. Optimization of the Reaction Conditions[a]



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

entry	additive (mol%)	oxidant (equiv)	solvent	temp (°C)	yield(%)[b]
1	$AgSbF_6$ (20)	$Cu(OAc)_2$ H_2O (2)	DCE	100	63
2	$AgBF_4$ (20)	$Cu(OAc)_2$ H_2O (2)	DCE	100	30
3	AgOTf (20)	$Cu(OAc)_2$ H_2O (2)	DCE	100	54
4	$AgNTf_2$ (20)	$Cu(OAc)_2$ H_2O (2)	DCE	100	61
5	AgOAc (20)	$Cu(OAc)_2$ H_2O (2)	DCE	100	-
6	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2)	DCE	100	68
7	$AgSbF_6$ (30)	Ag_2O (2)	DCE	100	23
8	$AgSbF_6$ (30)	BQ (2)	DCE	100	61
9	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (3)	DCE	100	56
10[c]	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2) + BQ (2)	DCE	100	79
11	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2) + BQ (2)	DCE	120	49
12	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2) + BQ (2)	DCE	80	46
13	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (0.5) + BQ (2)	DCE	100	52
14[d]	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2) + BQ (2)	DCE	100	77
15	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2) + BQ (2)	1,4-dioxane	100	49
16	$AgSbF_6$ (30)	$Cu(OAc)_2$ H_2O (2) + BQ (2)	TFE	100	65

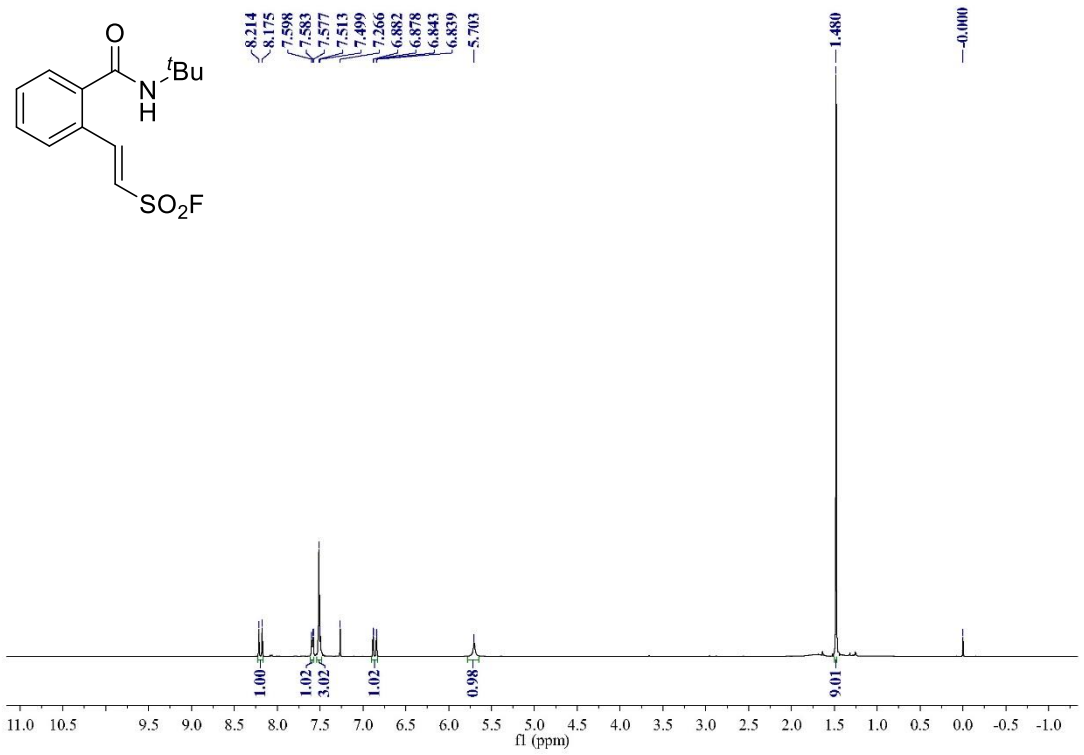
17	$AgSbF_6$ (30)	$Cu(OAc)_2 \cdot H_2O$ (2) + BQ (2)	MeCN	100	28
18	$AgSbF_6$ (30)	$Cu(OAc)_2 \cdot H_2O$ (2) + BQ (2)	DCM	100	46
19	$AgSbF_6$ (30)	$Cu(OAc)_2 \cdot H_2O$ (2) + BQ (2)	MeOH	100	trace

[a]Unless otherwise noted, reactions were conducted with **1a** (0.2 mmol), **2** (0.4 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), additive and oxidant in a solvent (2.0 mL) for 1 h. [b]Isolated yields. [c]BQ might be contribute to stabilization of the Ru species present in the catalytic cycle as a ligand similarly to the Pd-catalyzed reactions.[2] [d]under N_2.

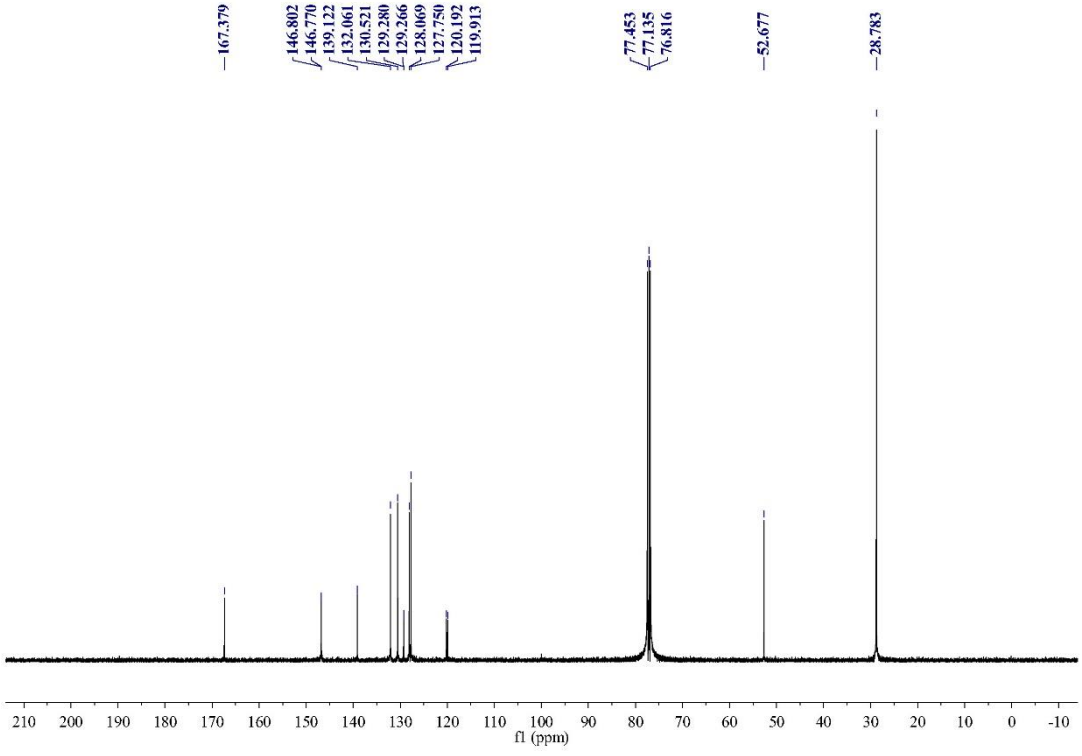
References

(1) Morales, S.; Guijarro, F. G.; Alonso, I.; García Ruano, J. L.; Cid, M. B. Dual Role of Pyrrolidine and Cooperative Pyrrolidine/Pyrrolidinium Effect in Nitrone Formation. *ACS Catal.* **2016**, *6*, 84-91.

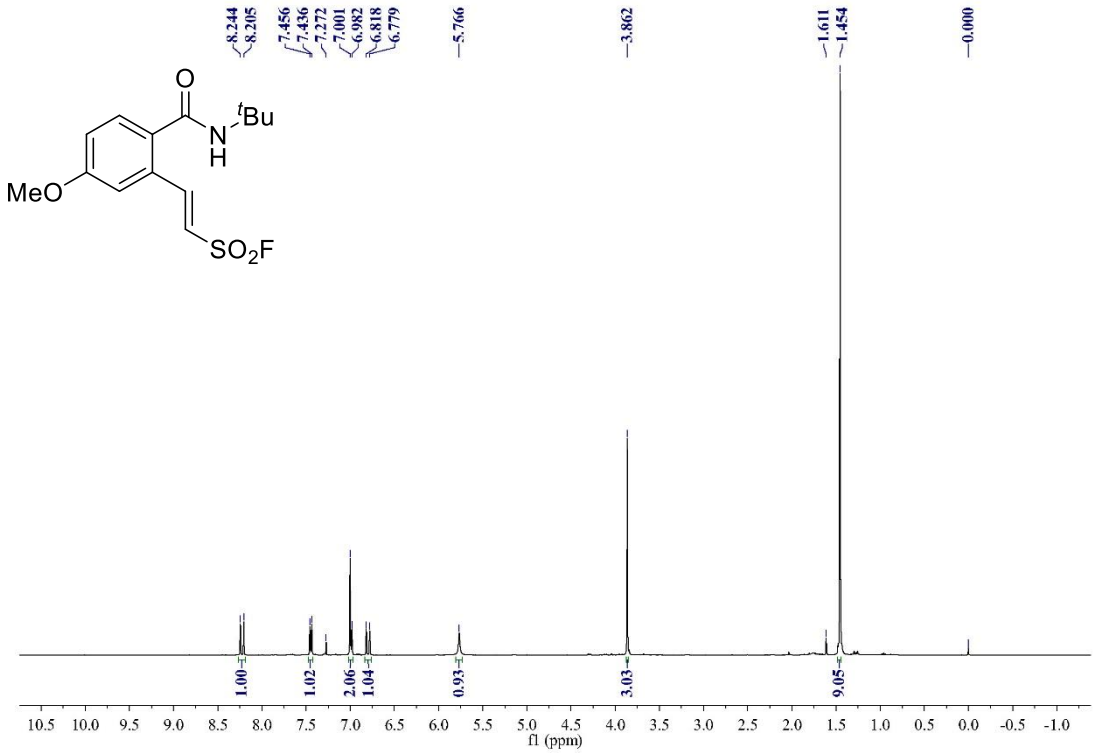
(2) (a) Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. Selective Pd-Catalyzed Oxidative Coupling of Anilides with Olefins through C-H Bond Activation at Room Temperature. *J. Am. Chem. Soc.* **2002**, *124*, 1586-1587. (b) Chu, J.-H.; Lin, P.-S.; Lee, Y.-M.; Shen, W.-T.; Wu, M.-J. Palladium(II)-Catalyzed One-Pot Syntheses of 9-(Pyridin-2-yl)-9H-carbazoles through a Tandem C-H Activation/C-X (X= C or N) Formation Process. *Chem. Eur. J.* **2011**, *17*, 13613-13620.



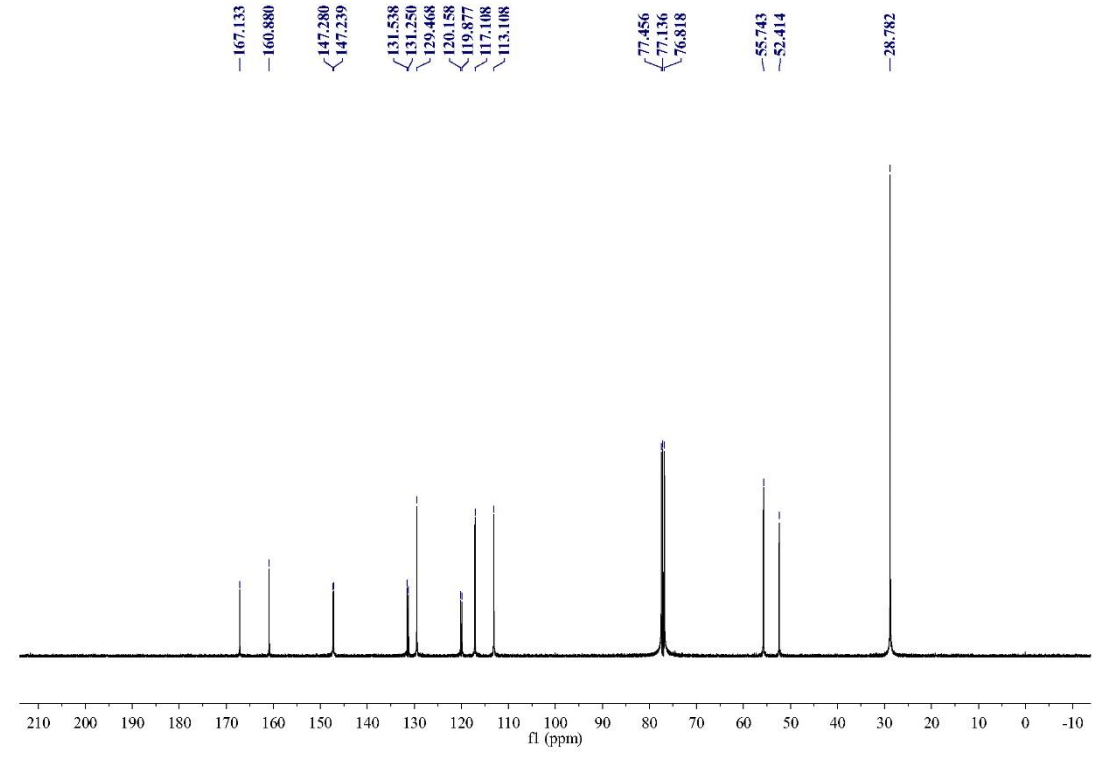
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3a**



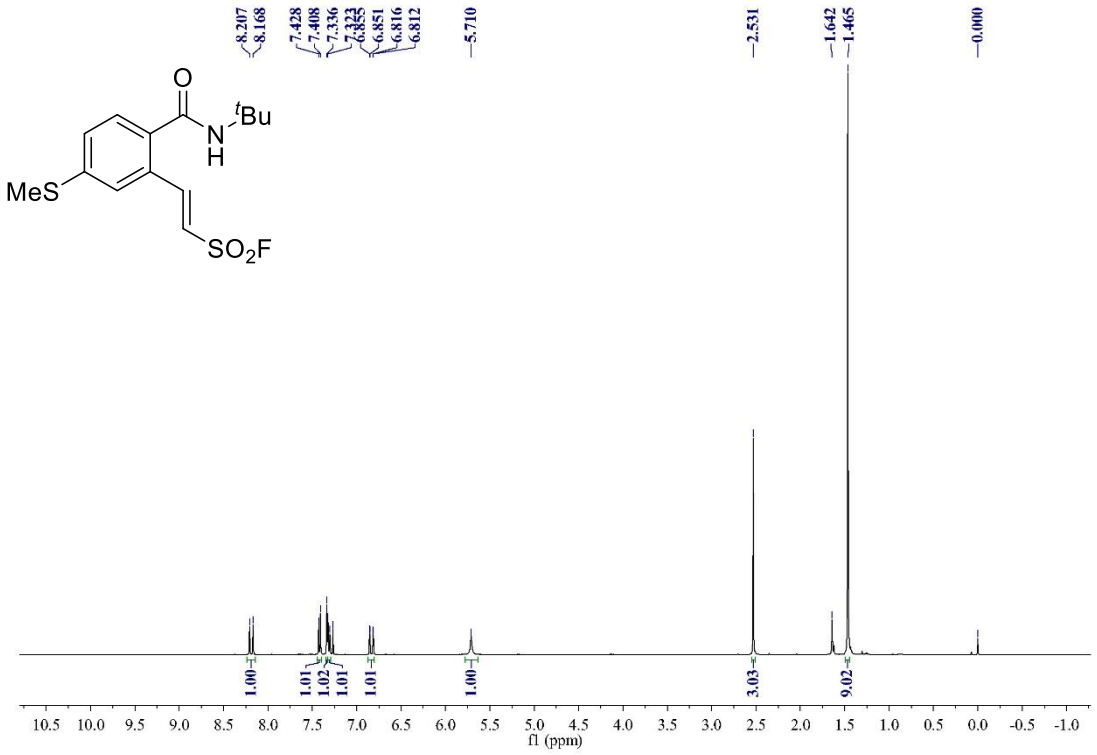
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3a**



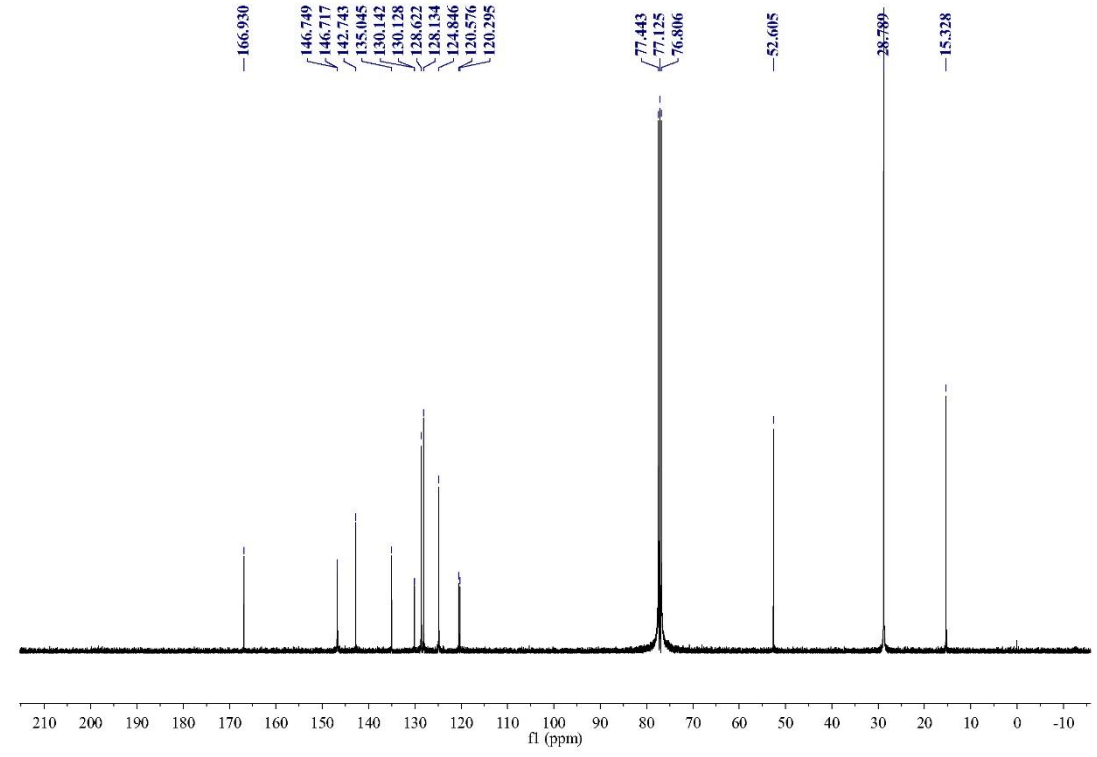
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3b**



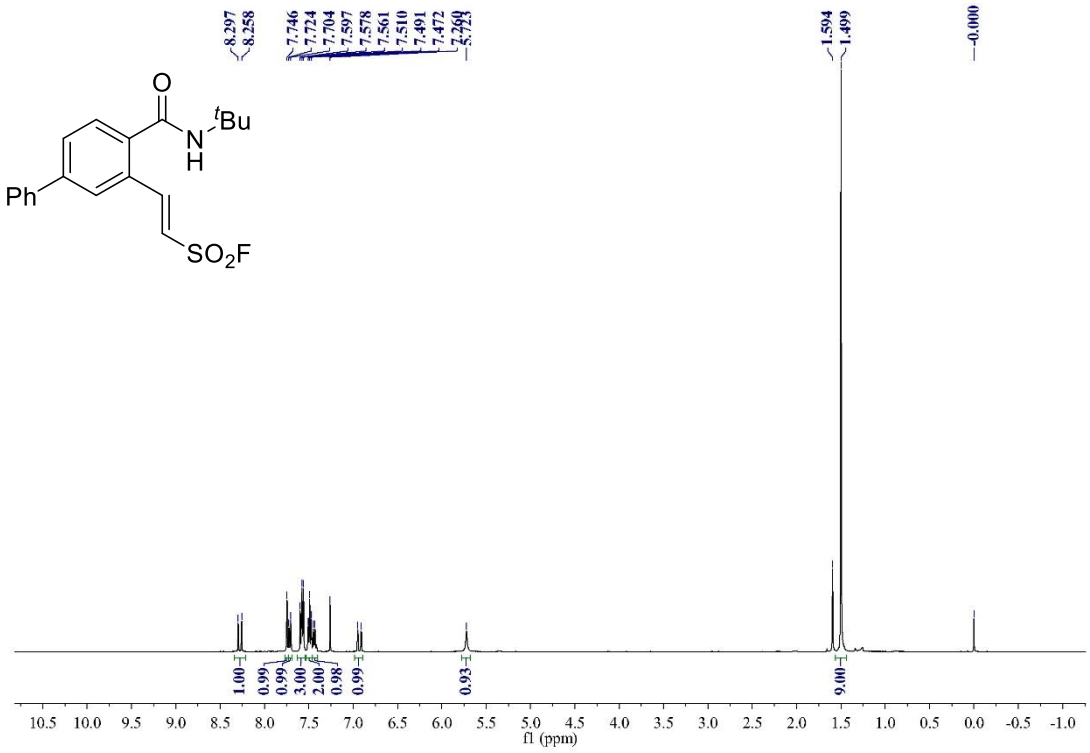
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3b**



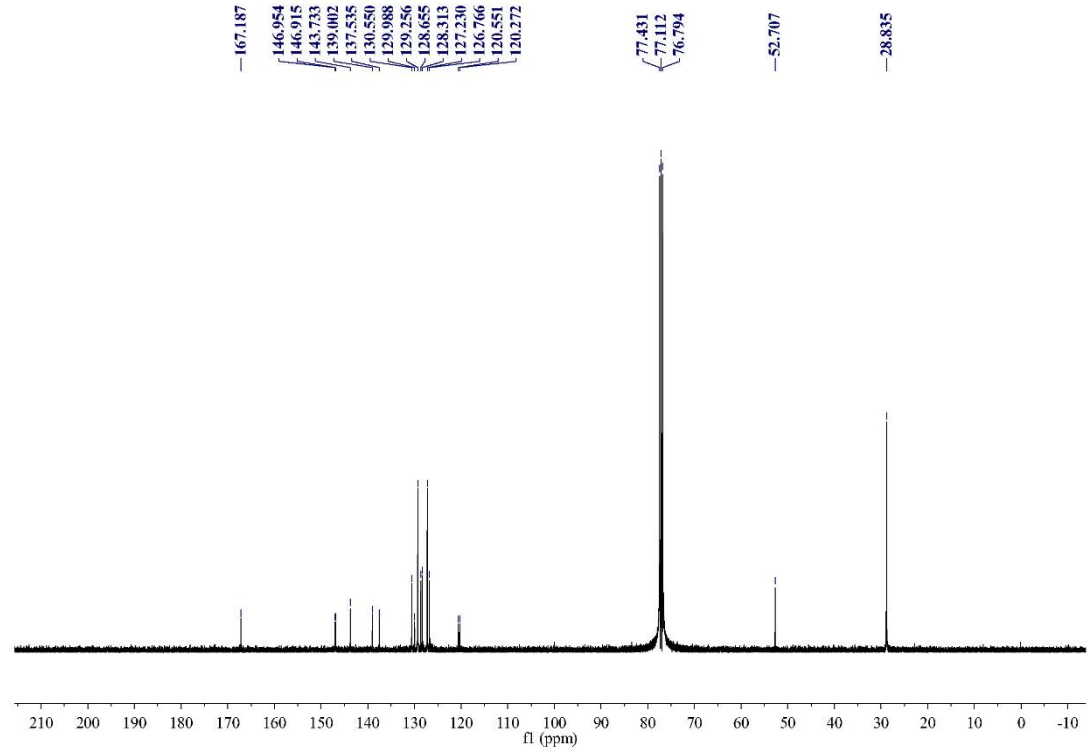
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3c**



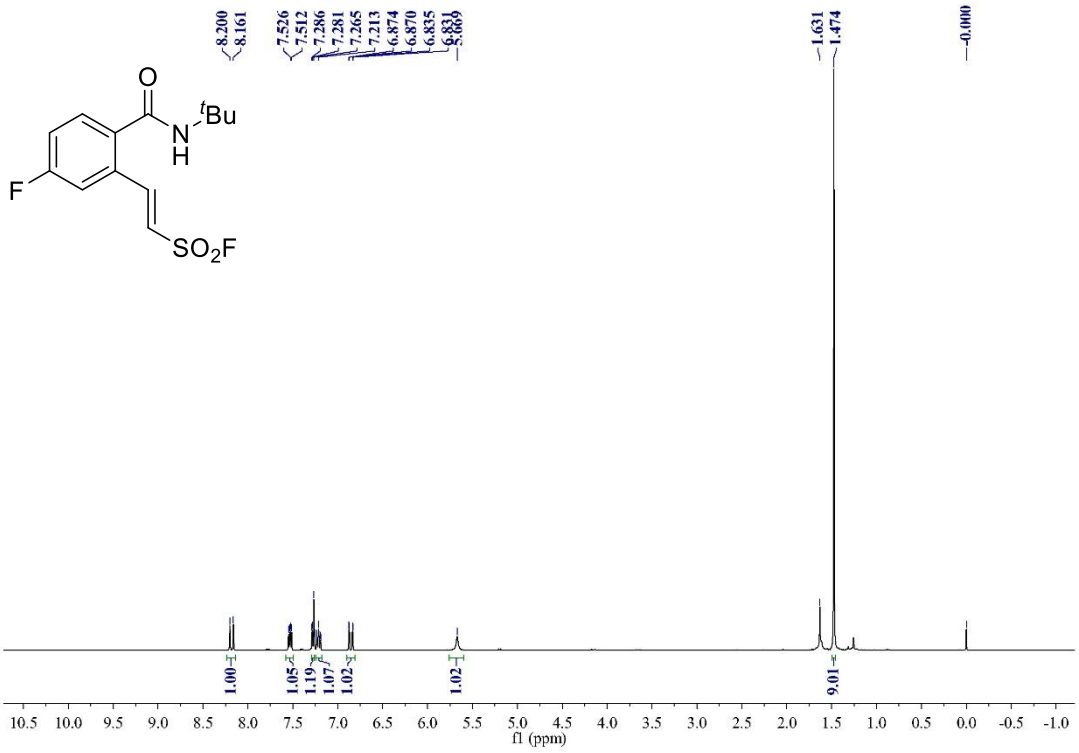
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3c**



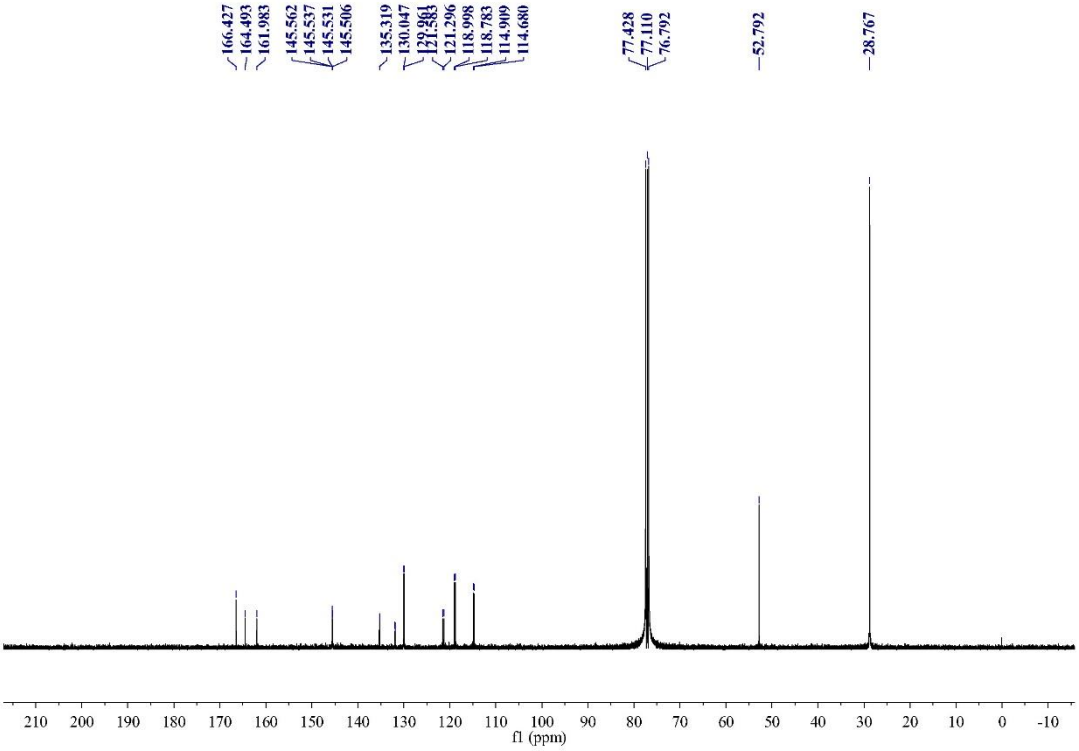
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3d**



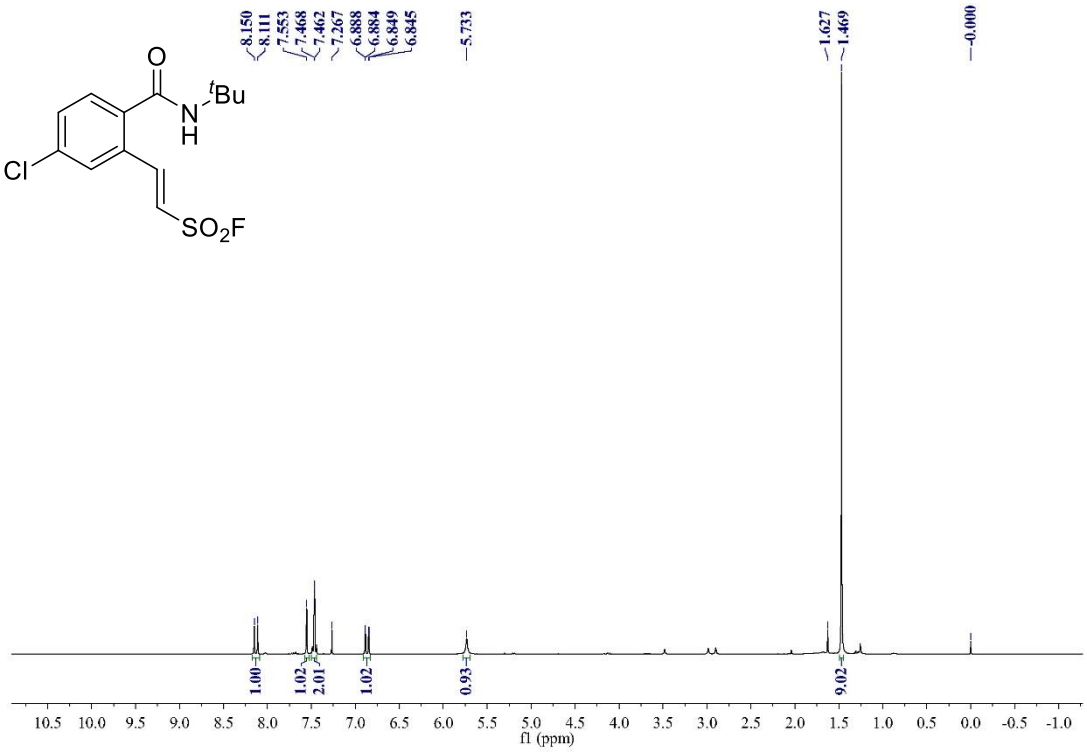
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3d**



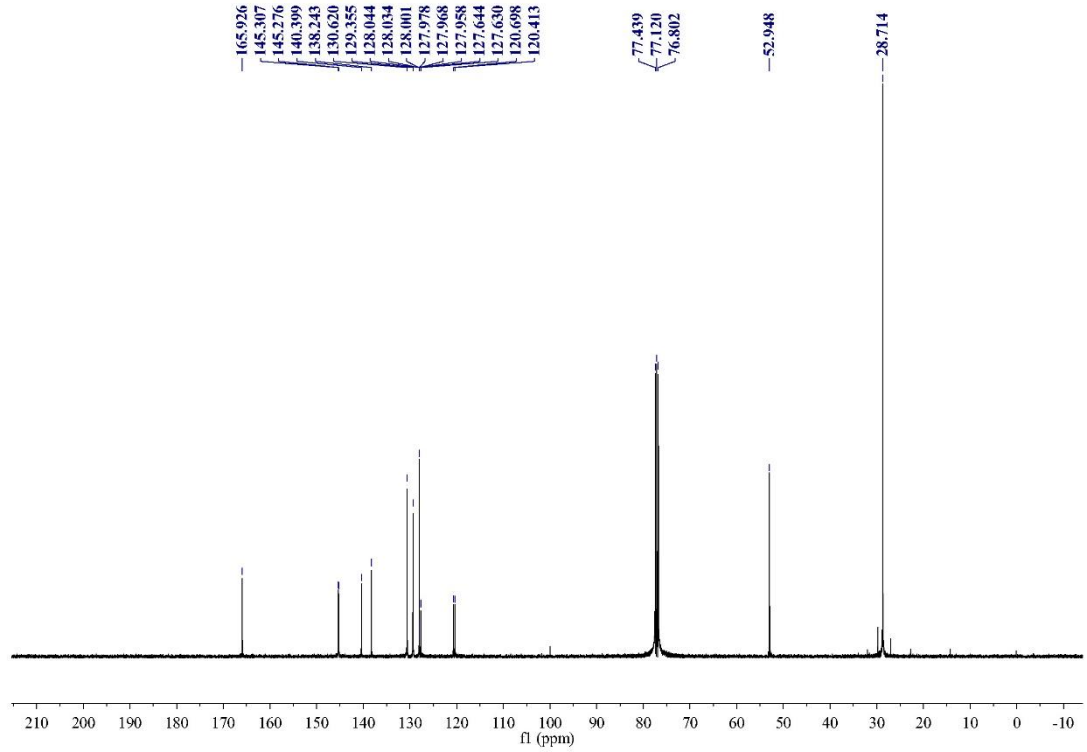
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3e**



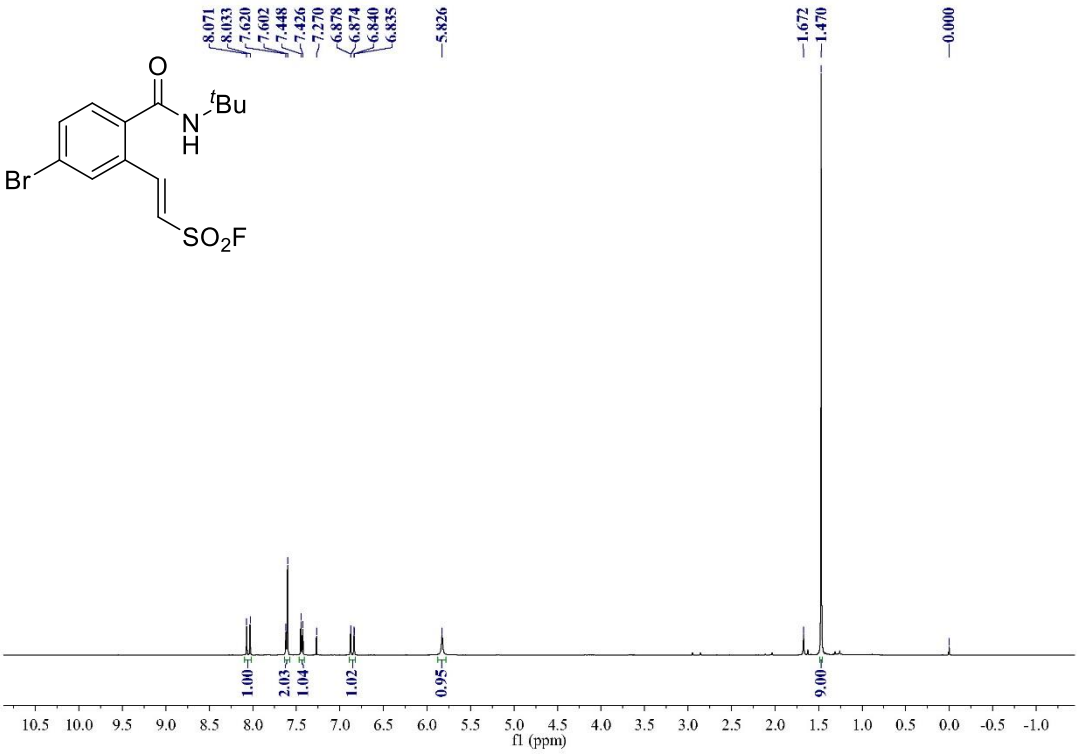
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3e**



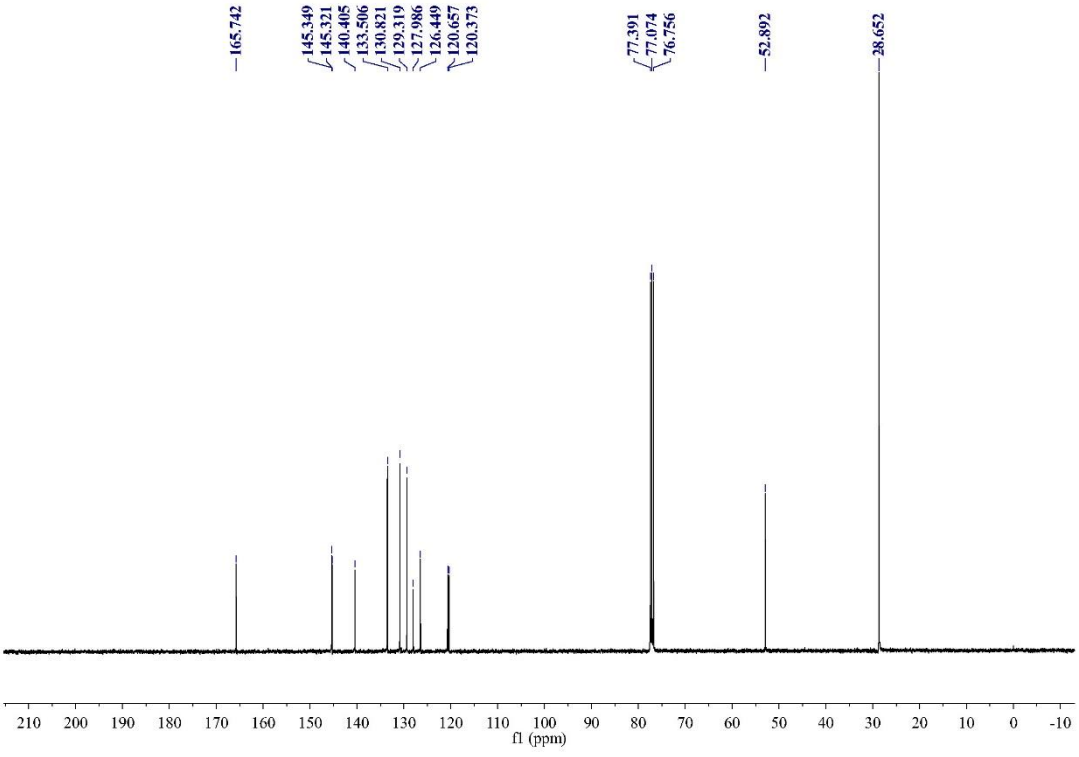
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3f**



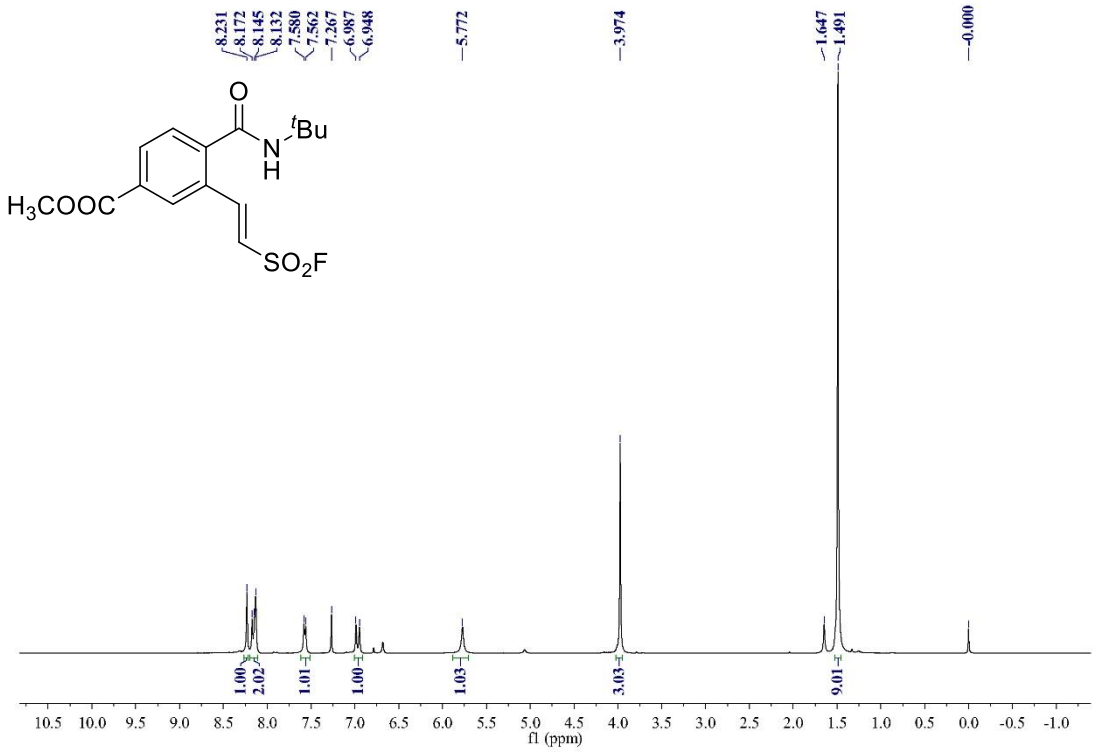
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3f**



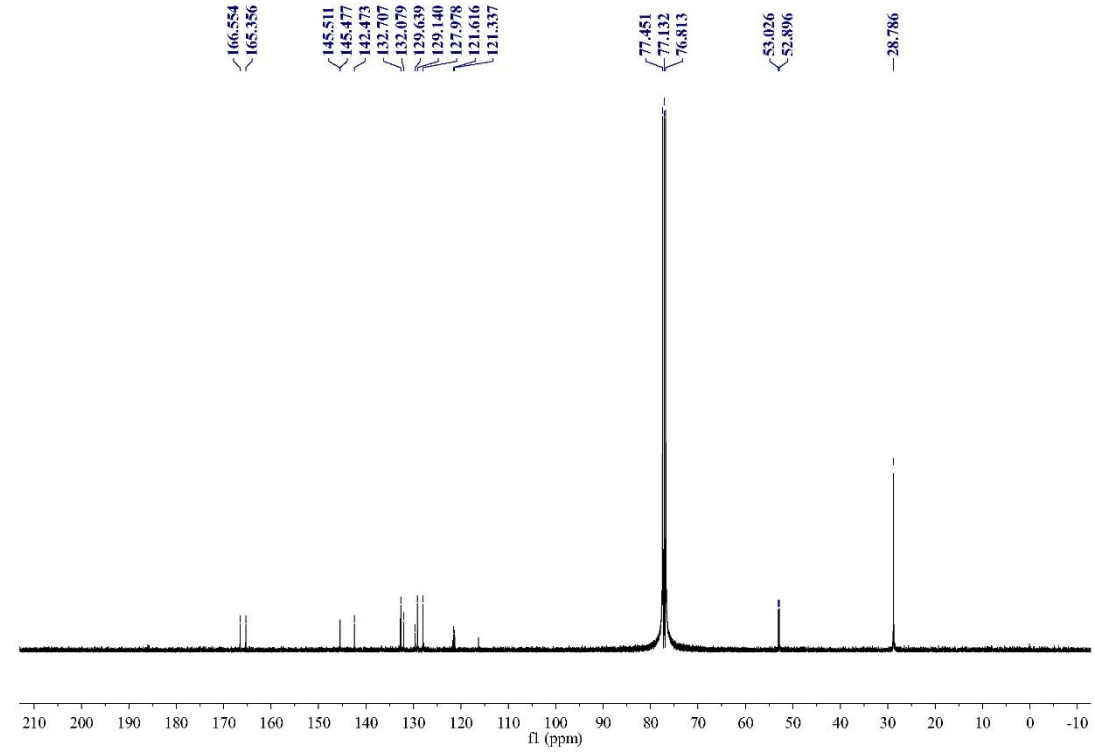
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3g**



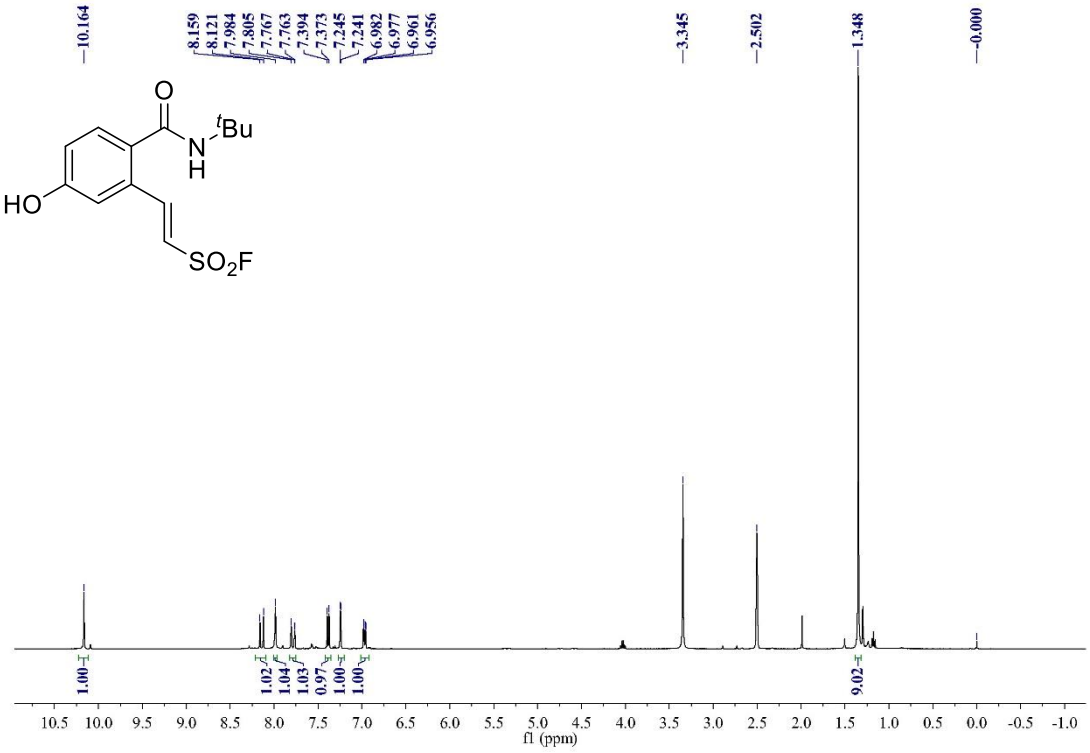
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3g**



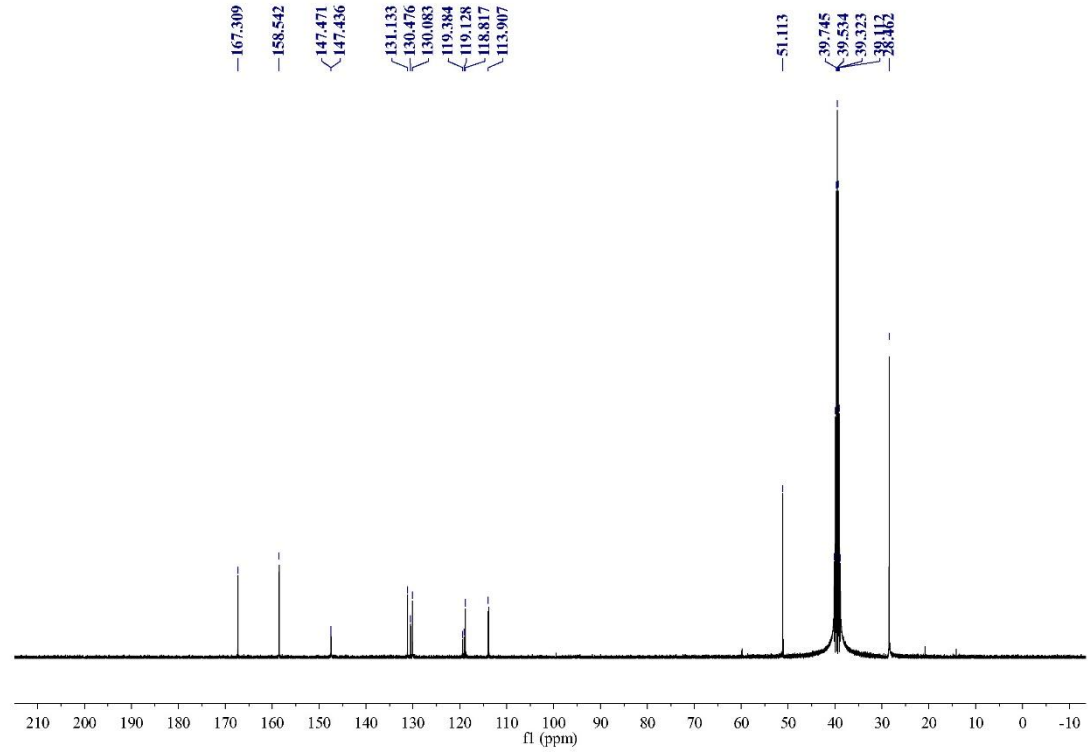
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3h**



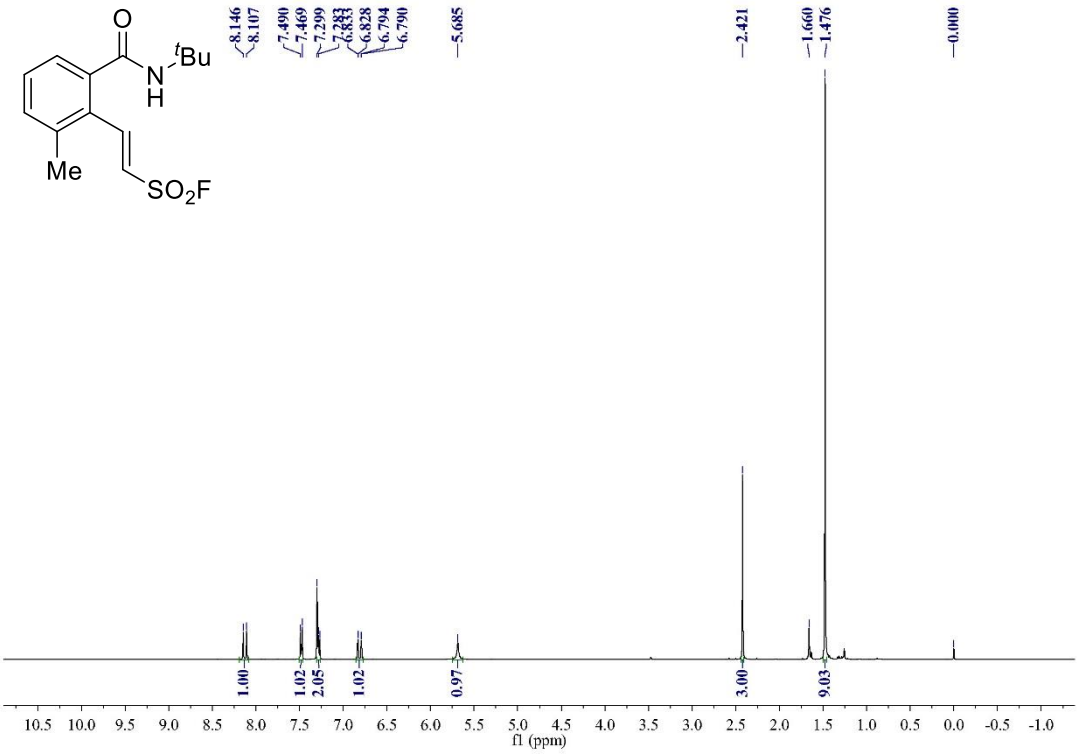
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3h**



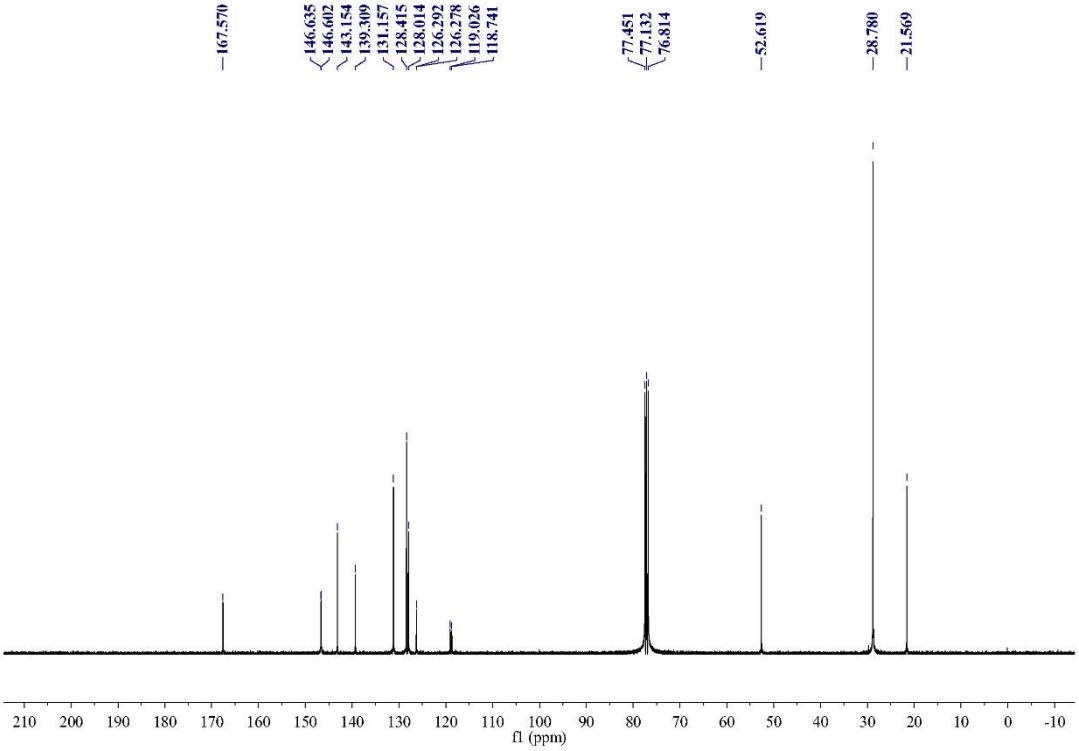
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3i**



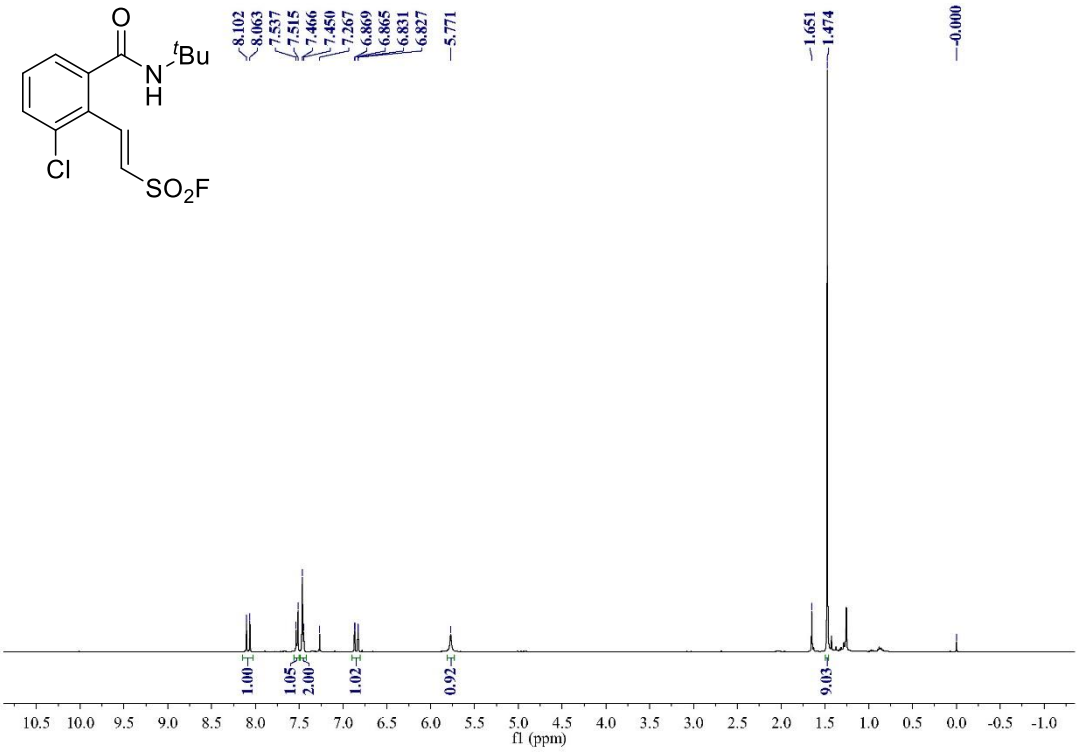
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3i**



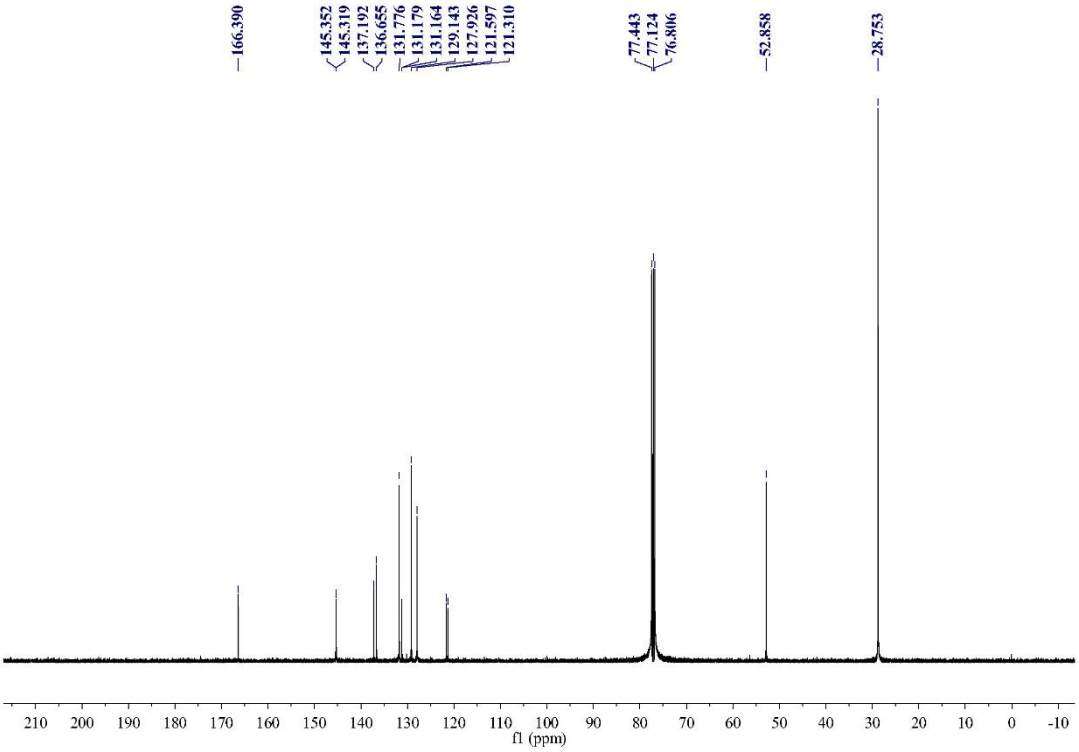
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3j**



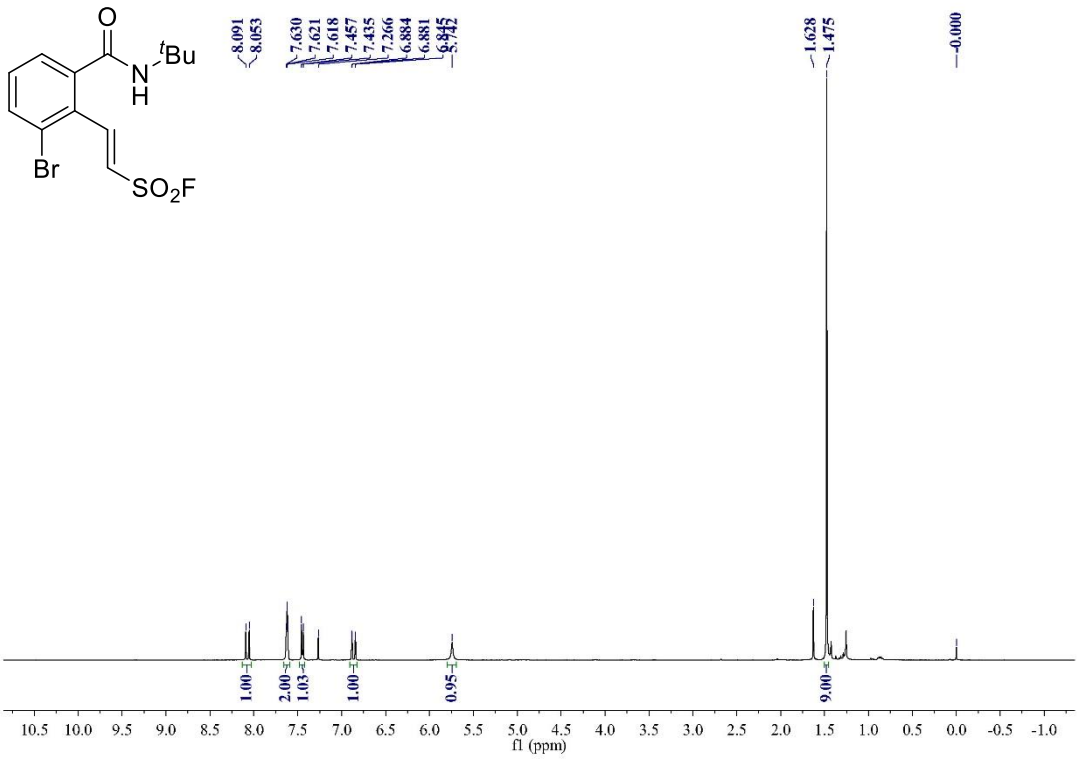
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3j**



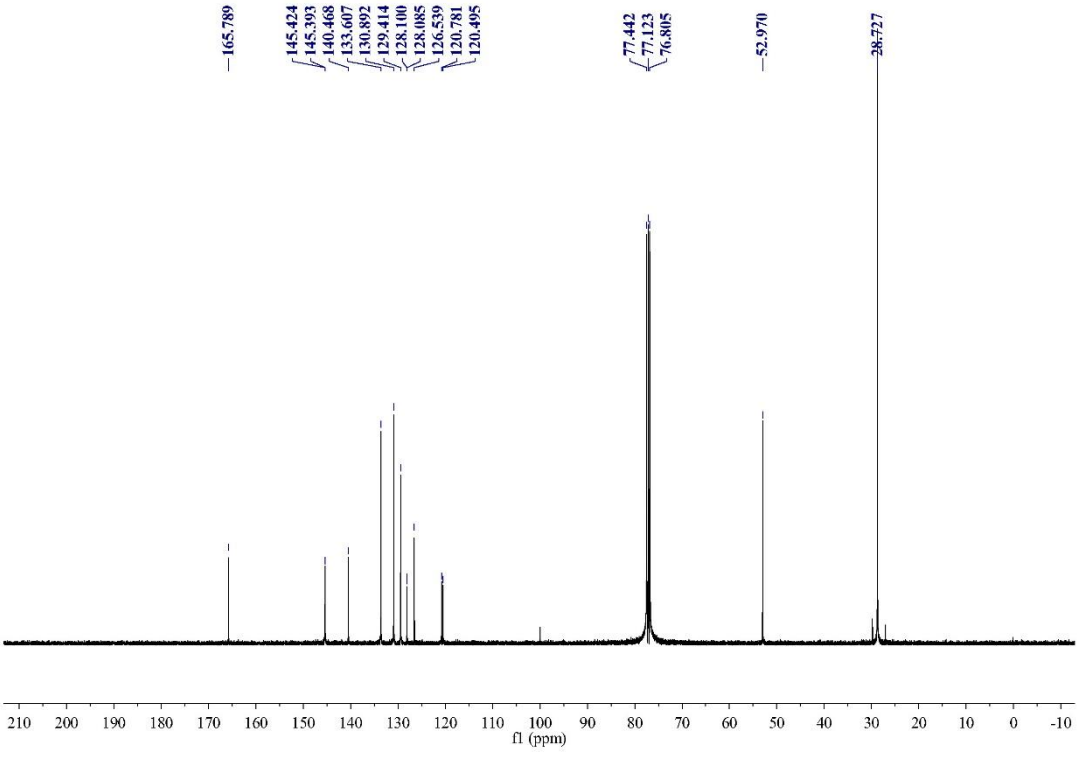
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3k**



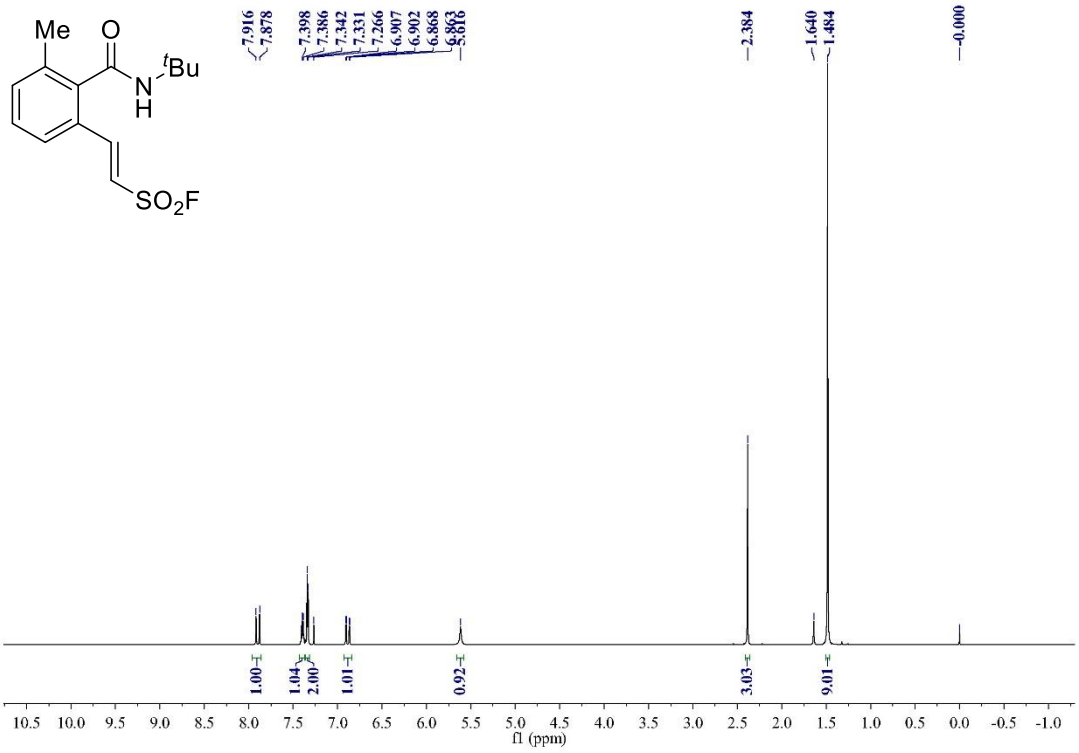
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3k**



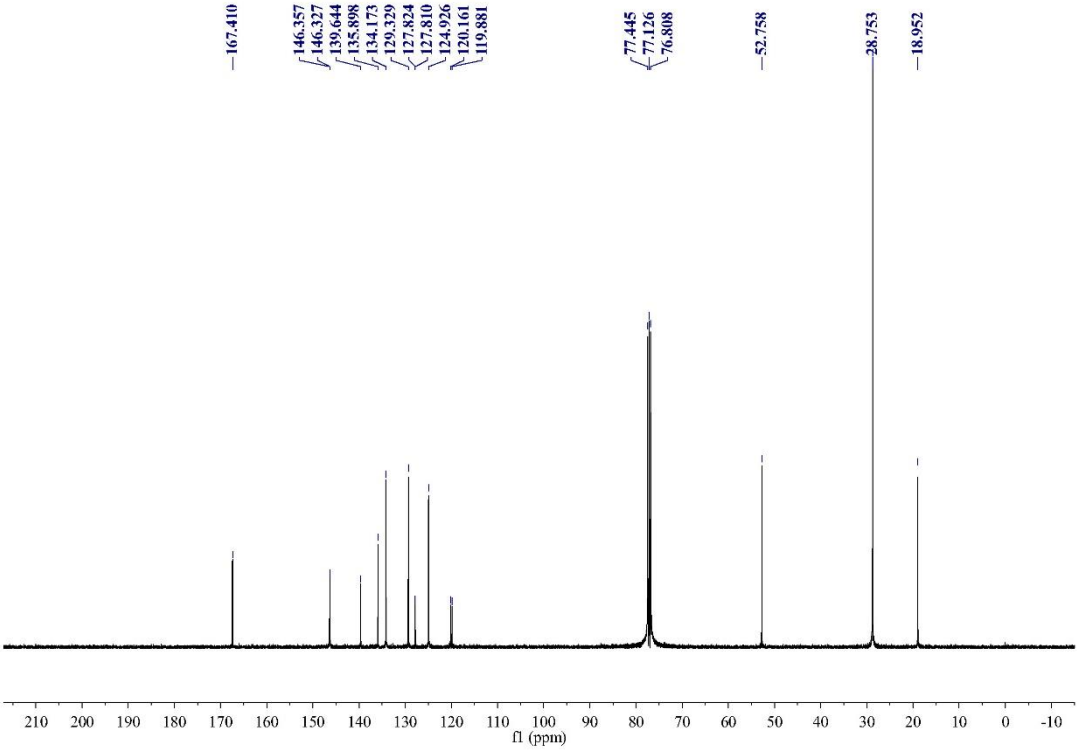
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3l**



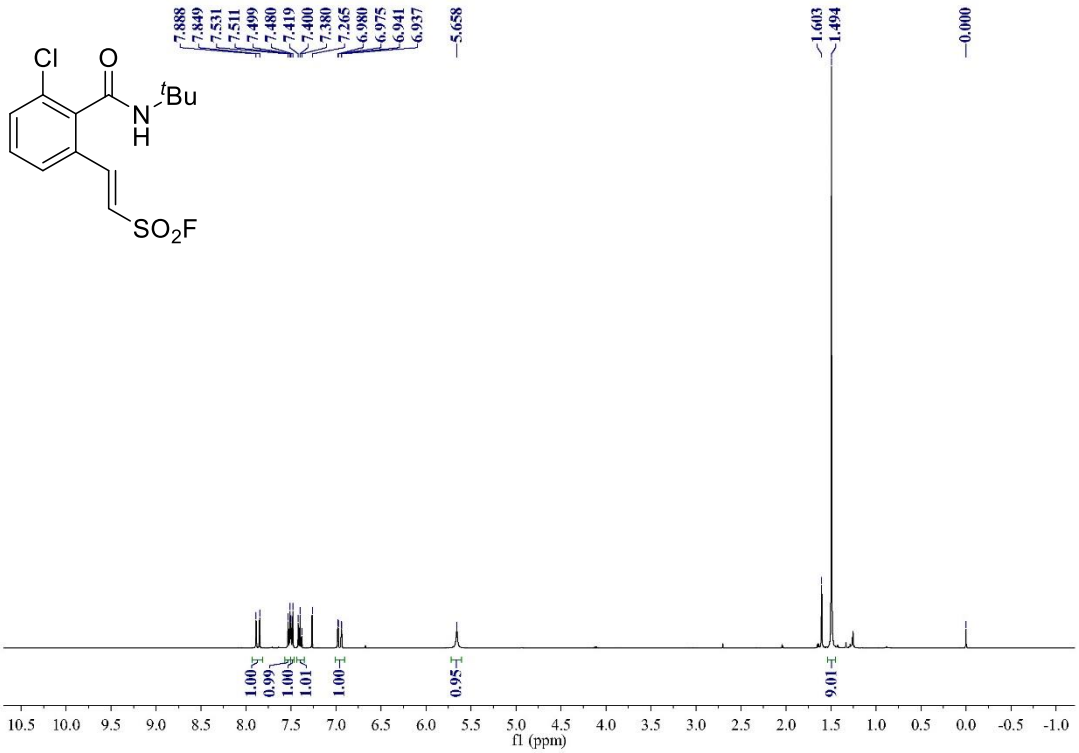
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3l**



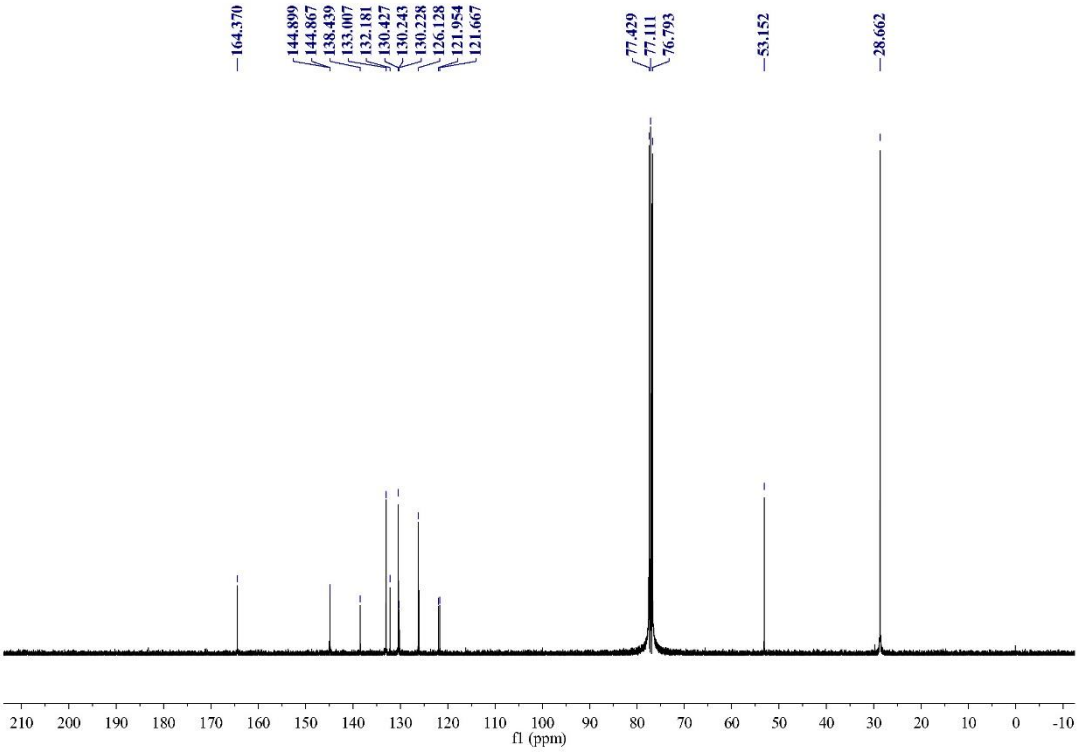
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3m**



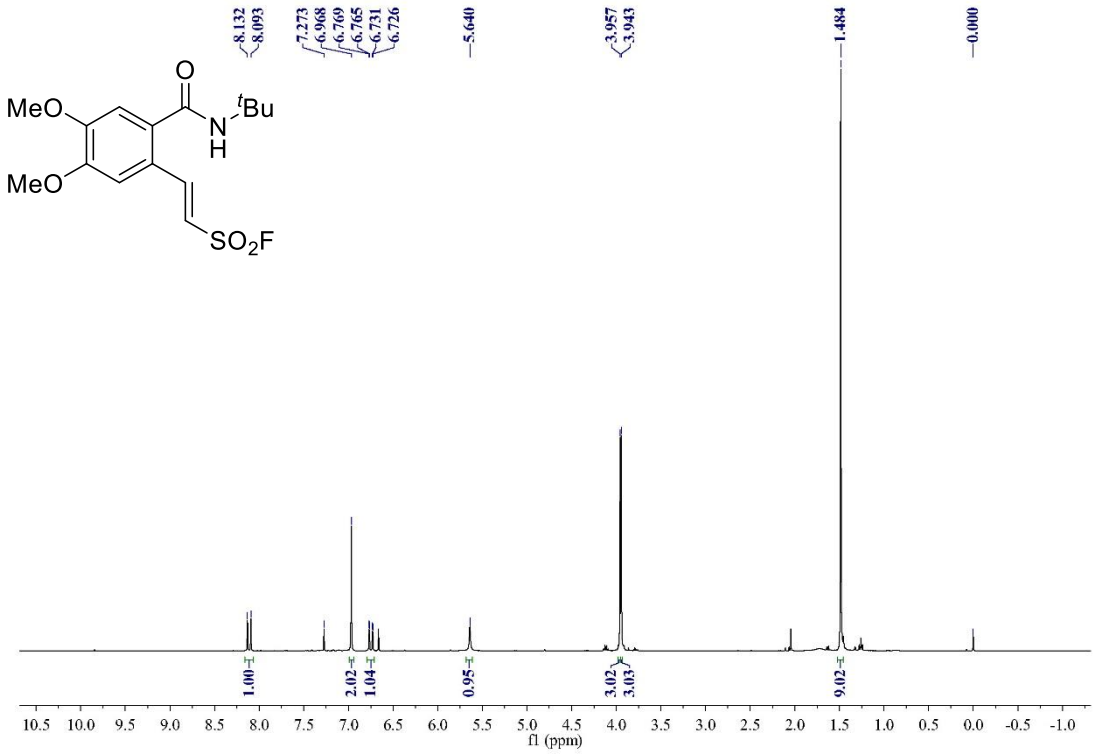
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3m**



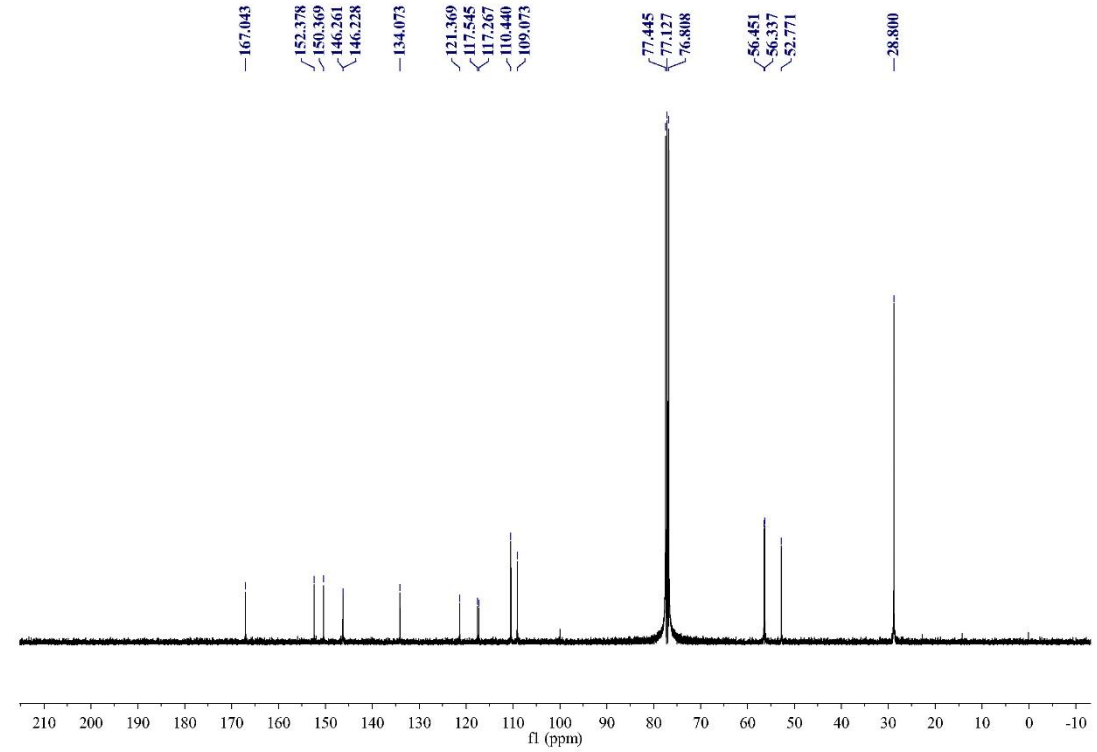
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3n**



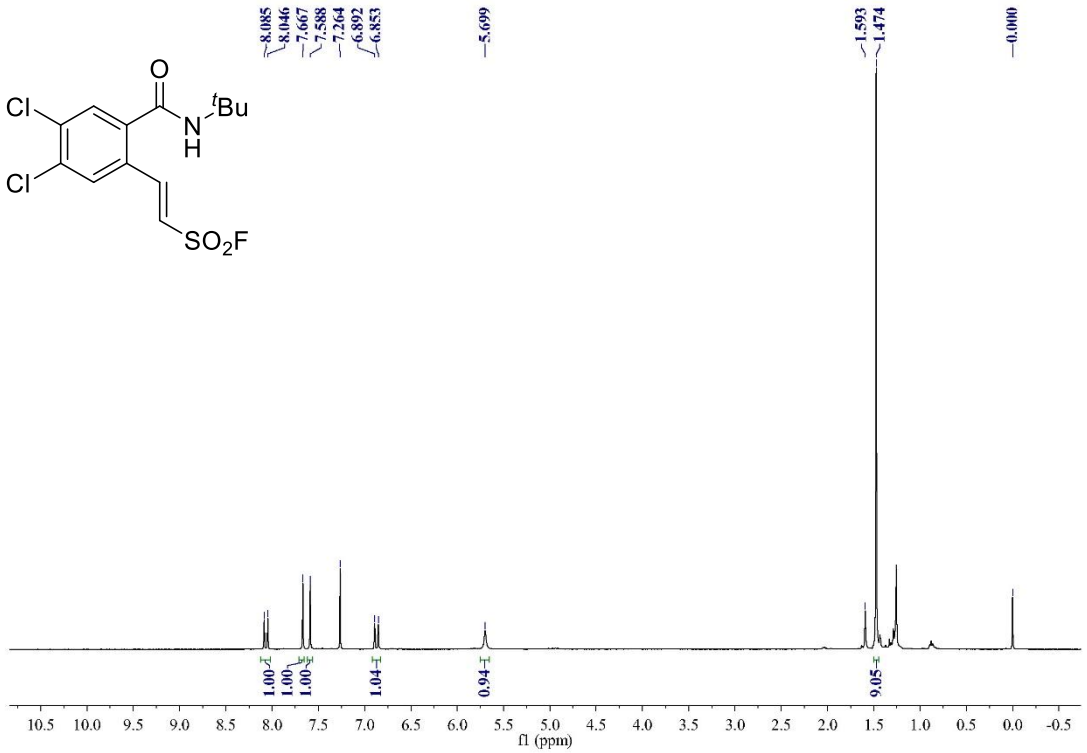
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3n**



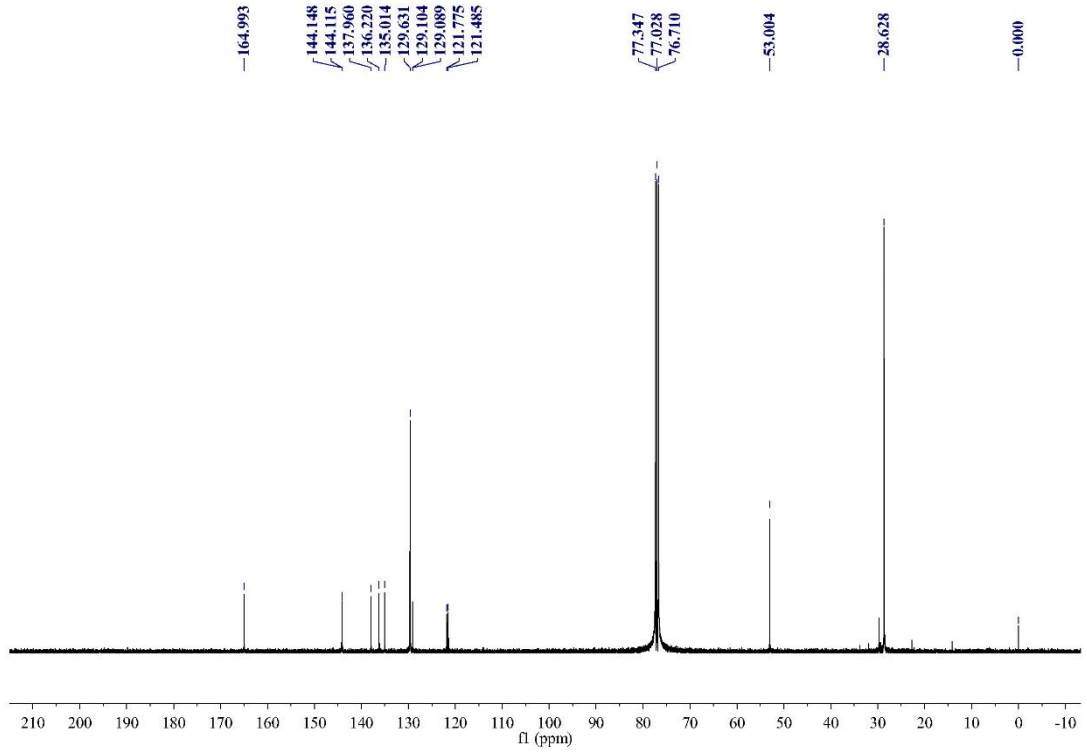
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3o**



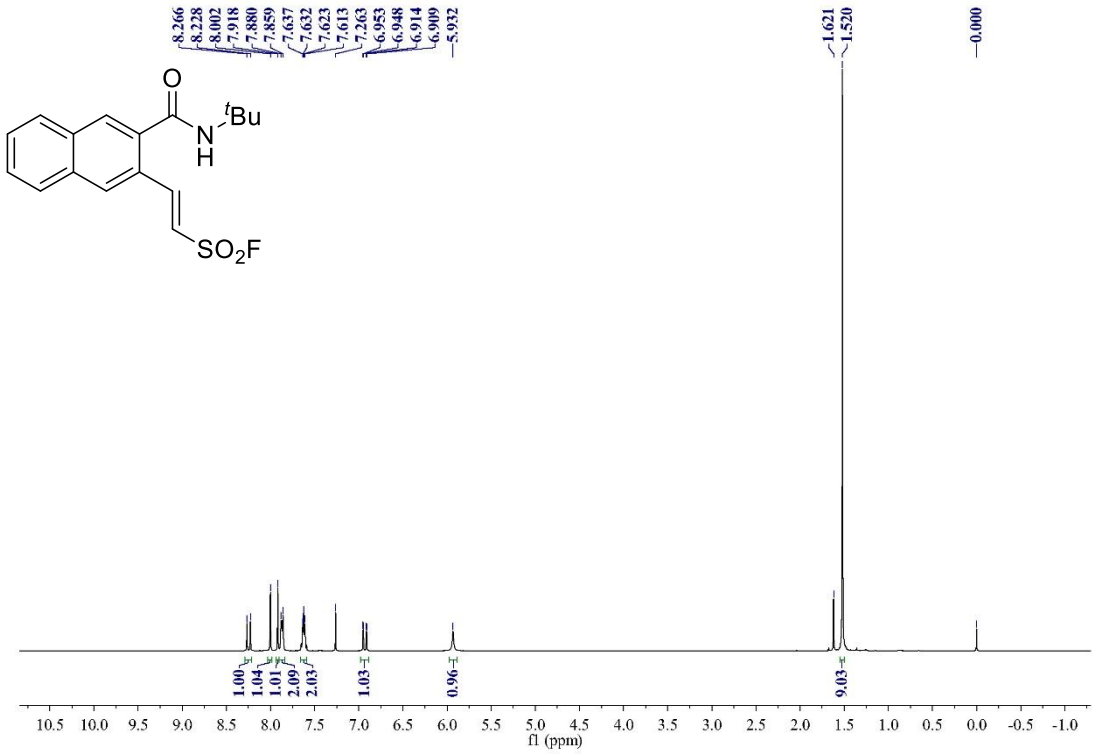
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3o**



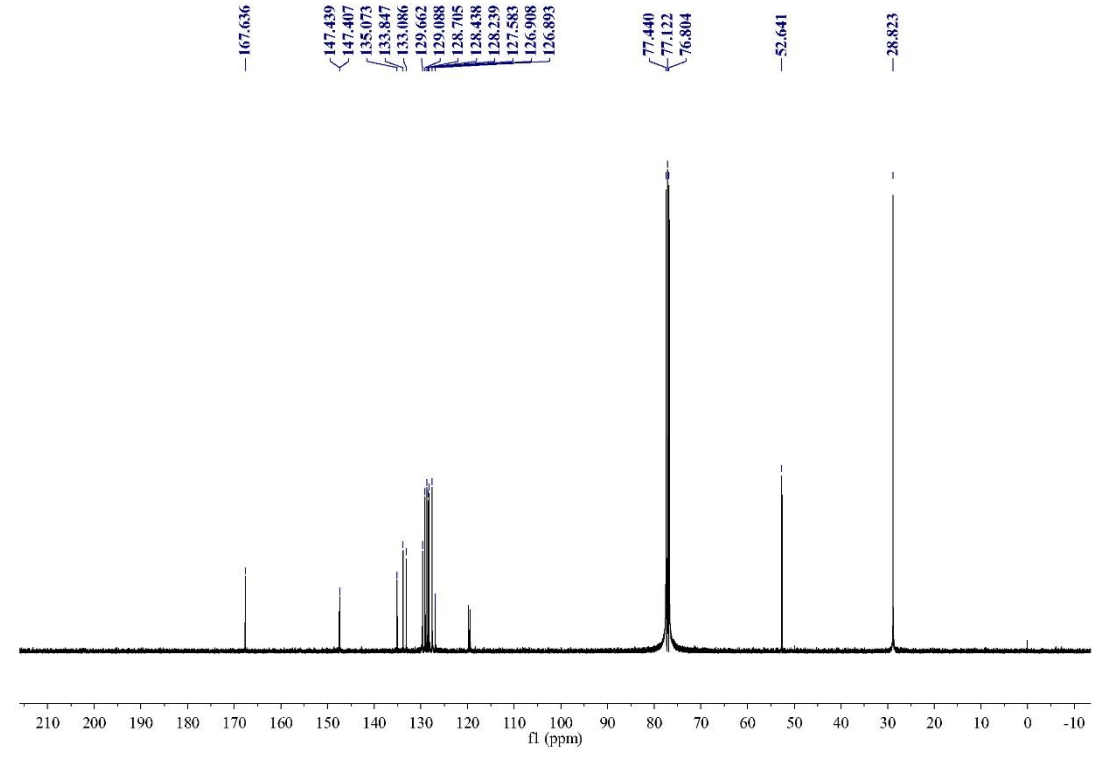
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3p**



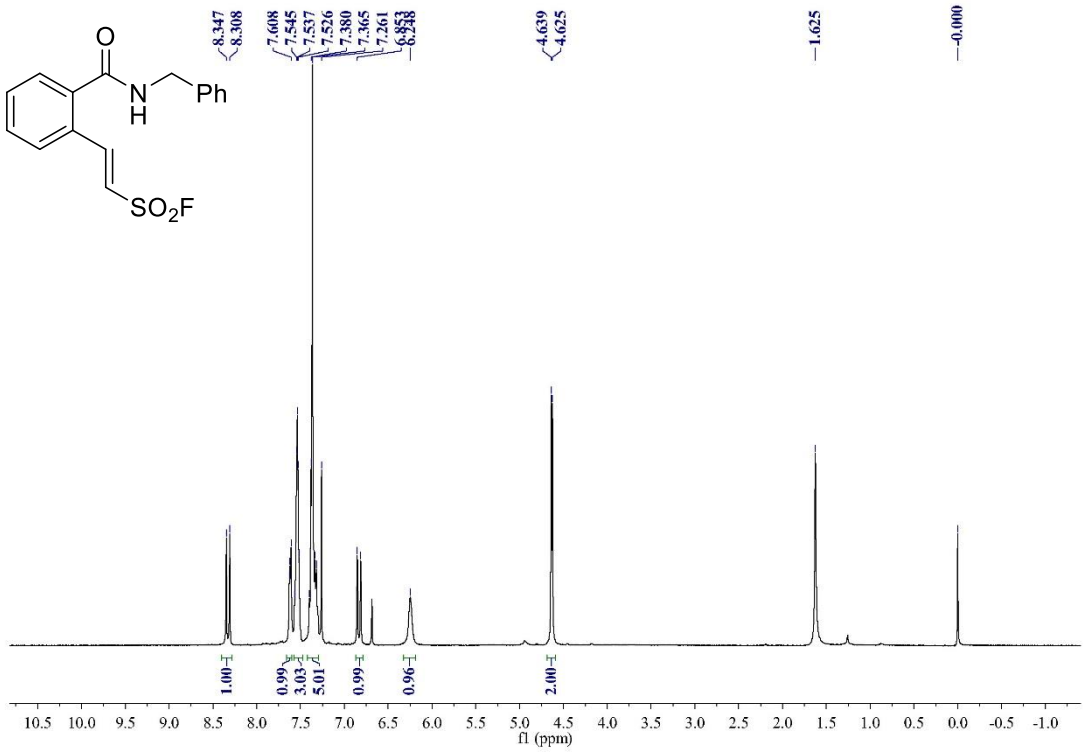
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3p**



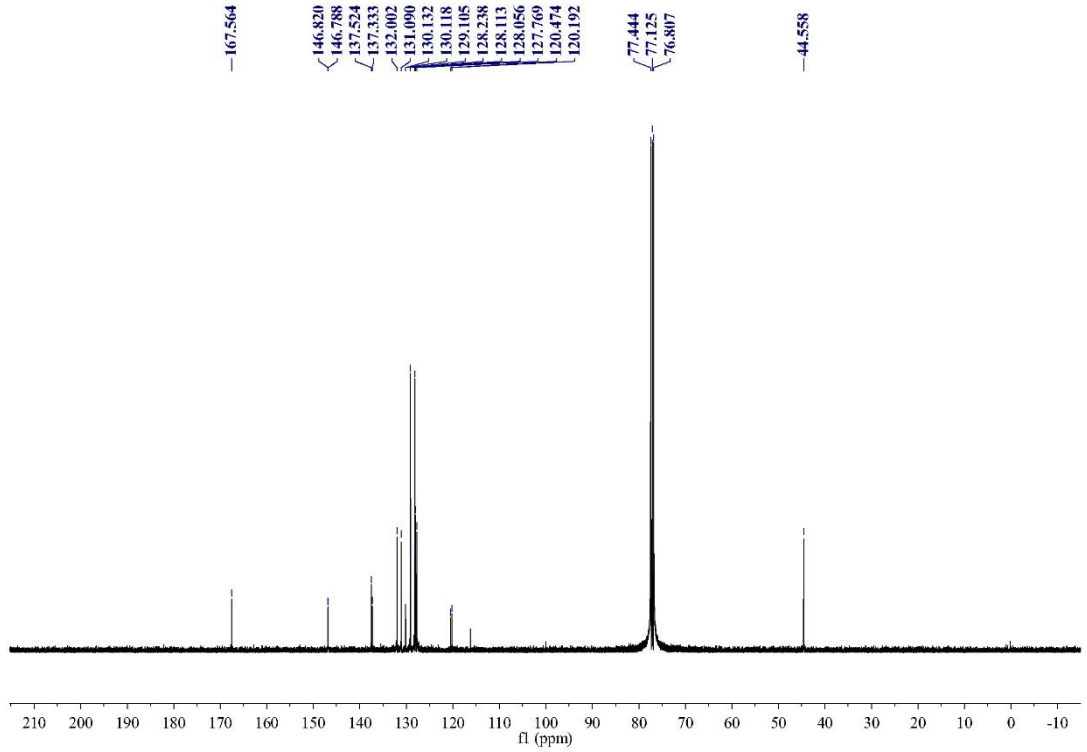
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3q**



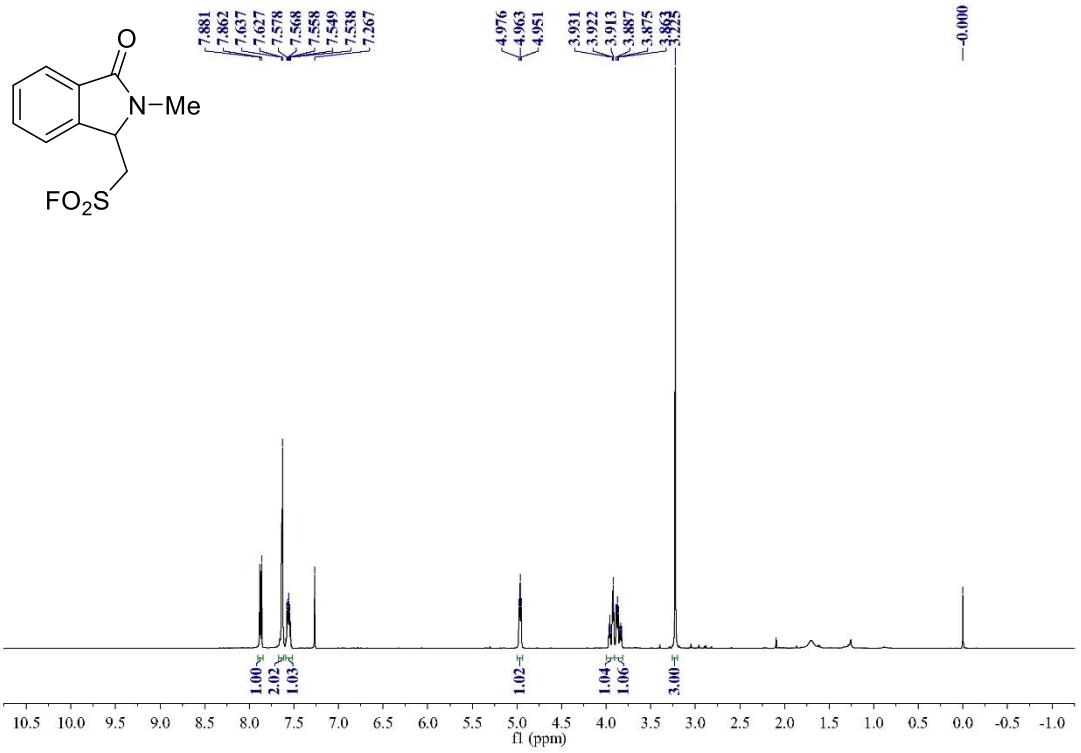
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3q**



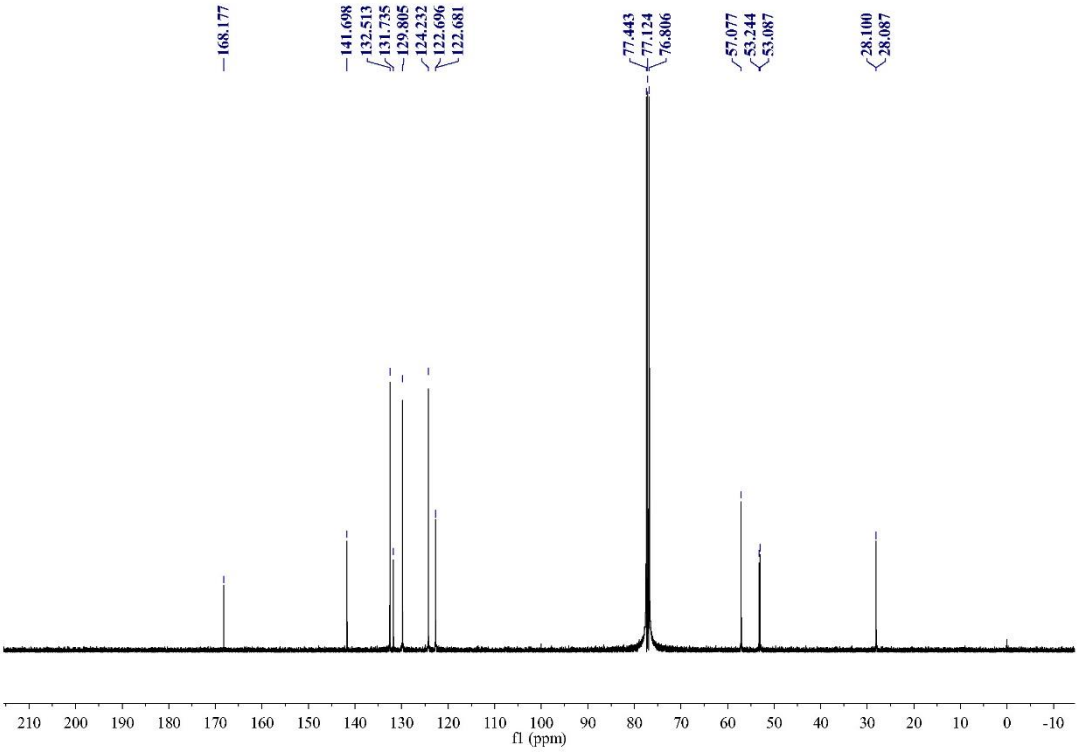
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3s**



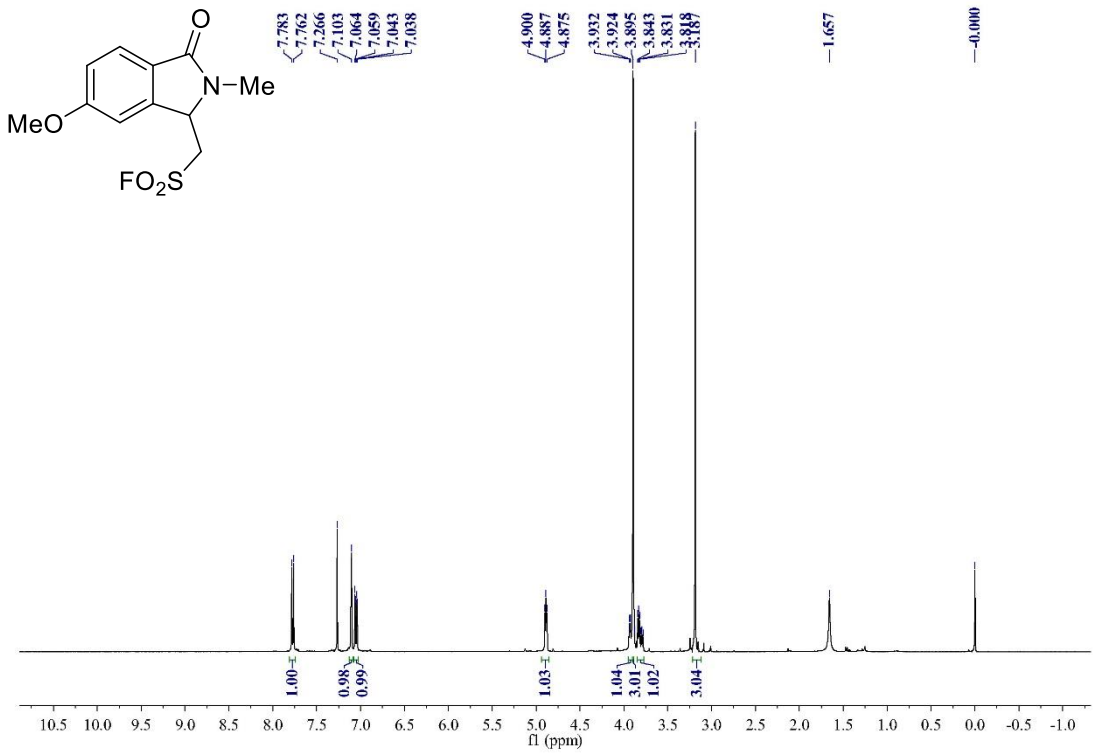
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3s**



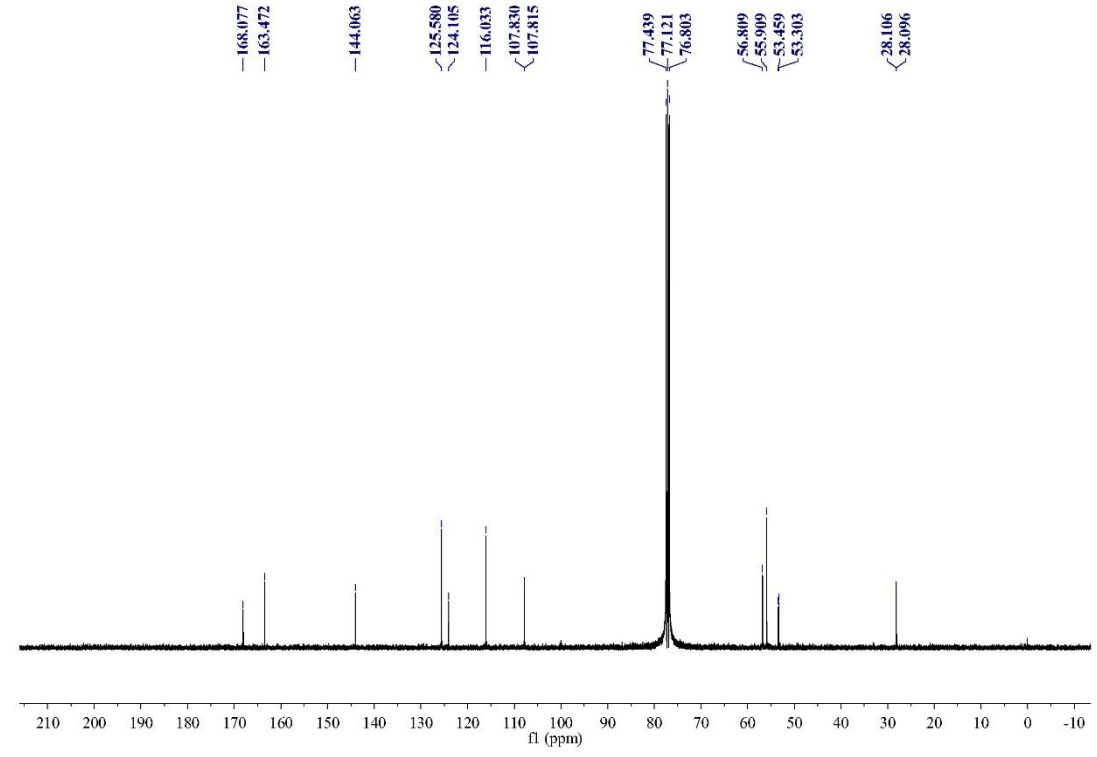
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5a**



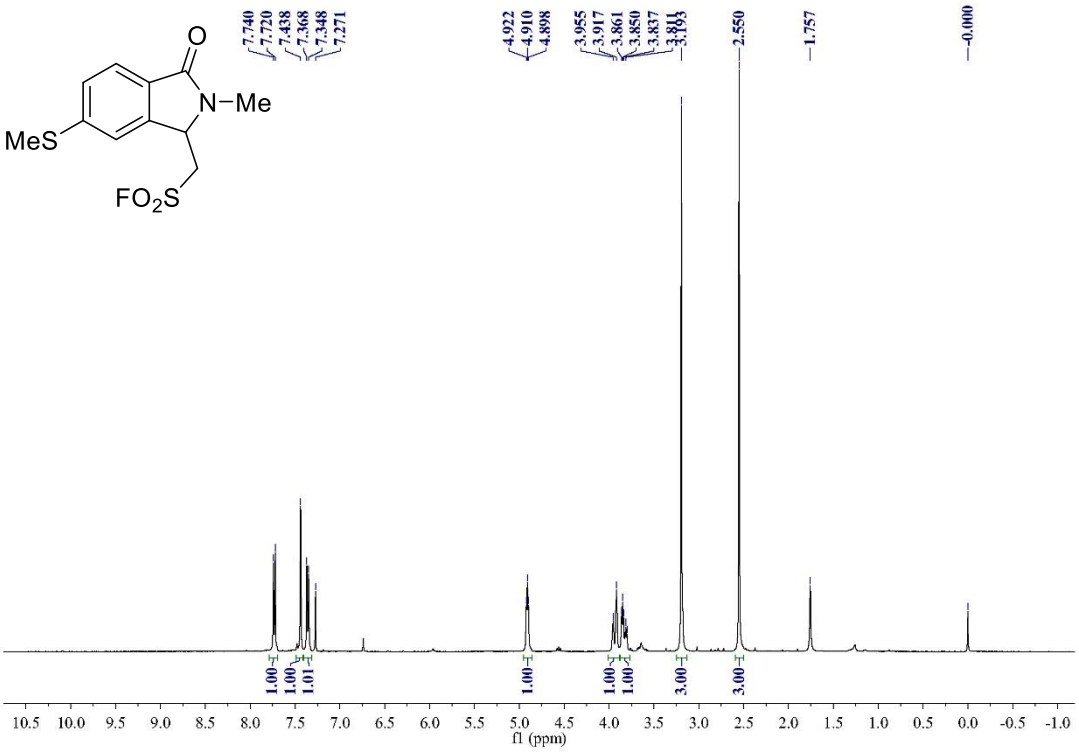
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5a**



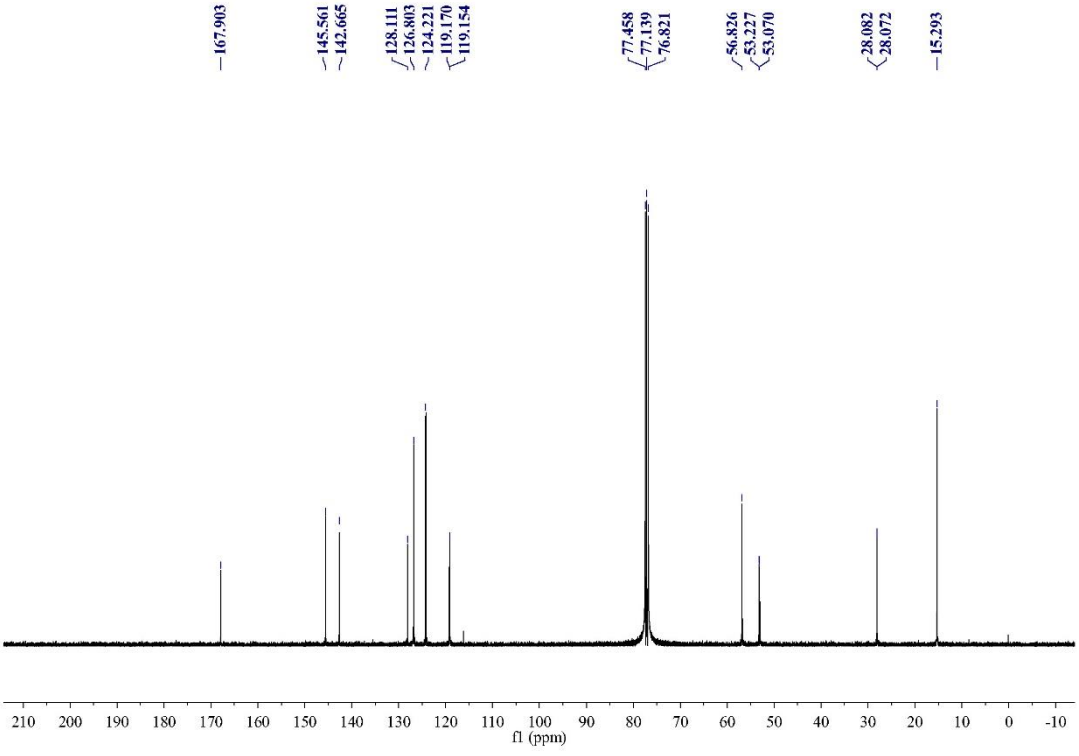
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5b**



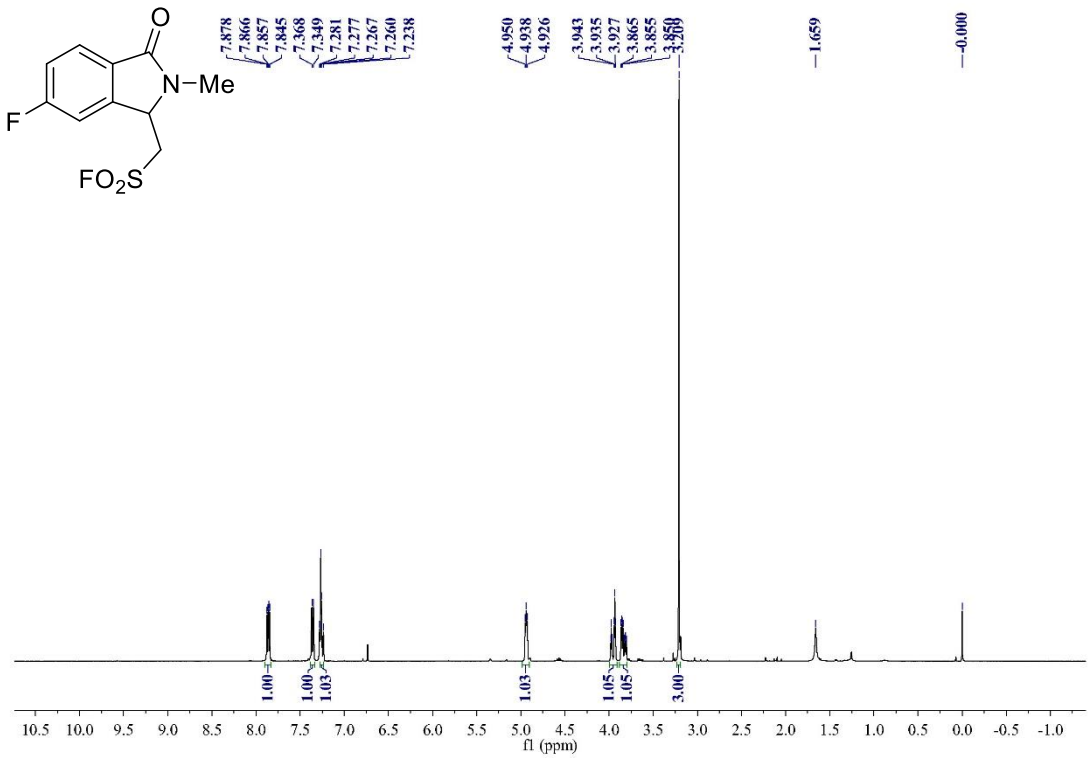
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5b**



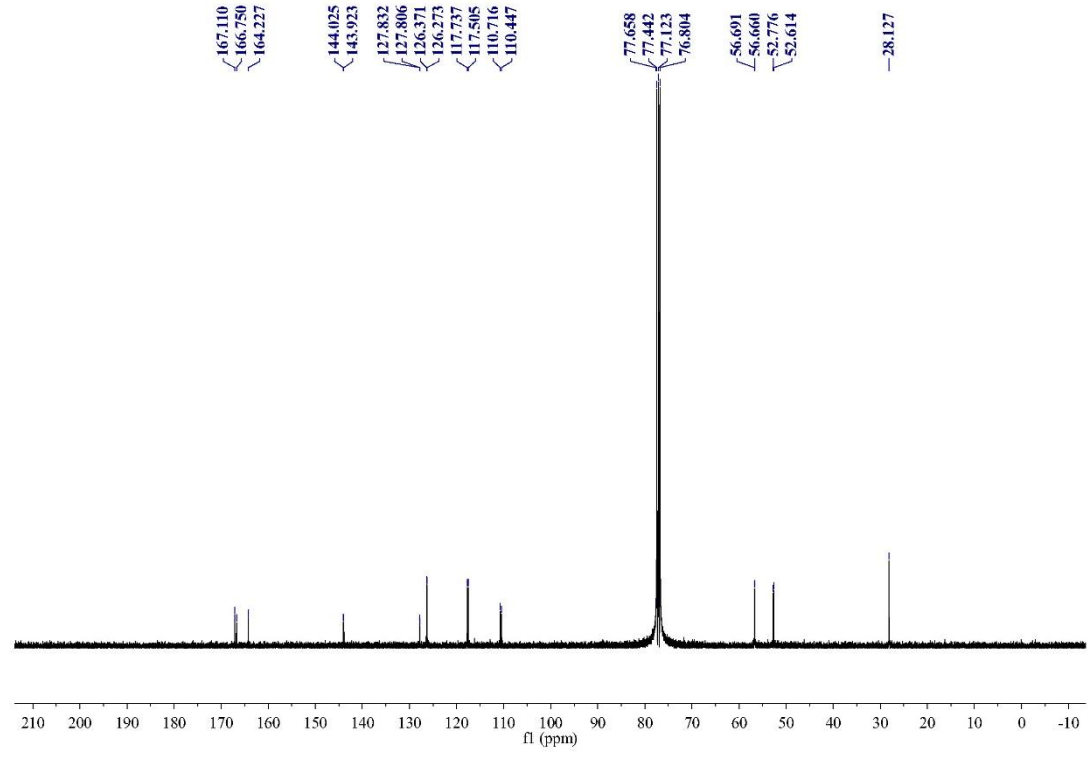
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5c**



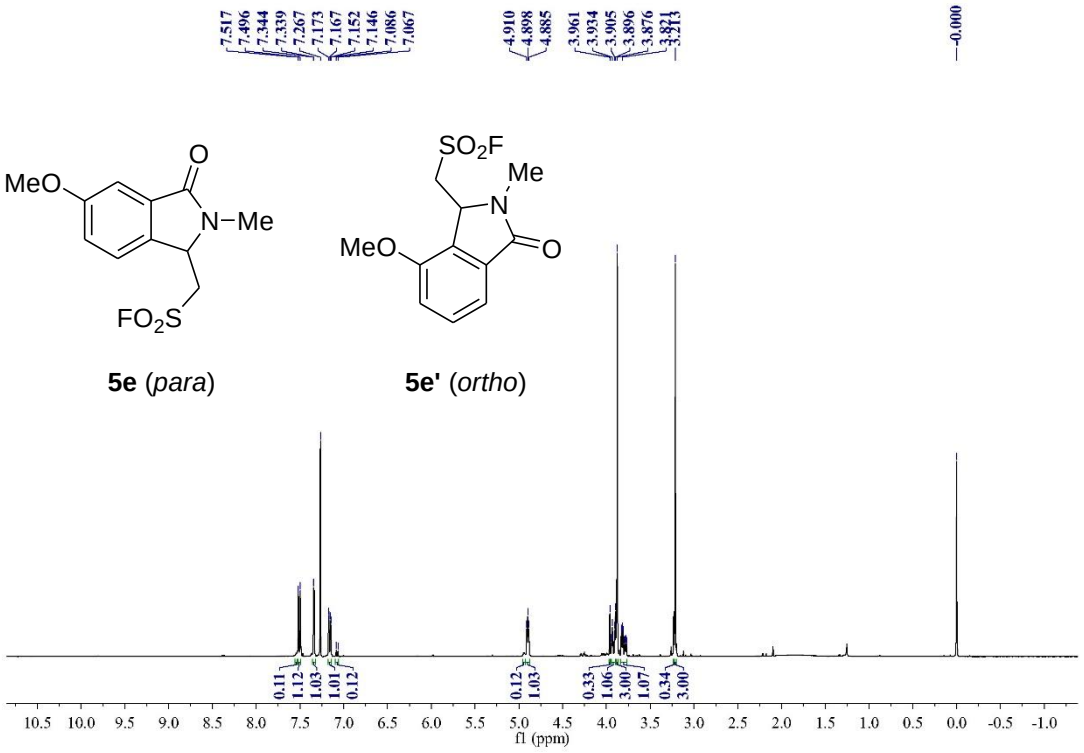
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5c**



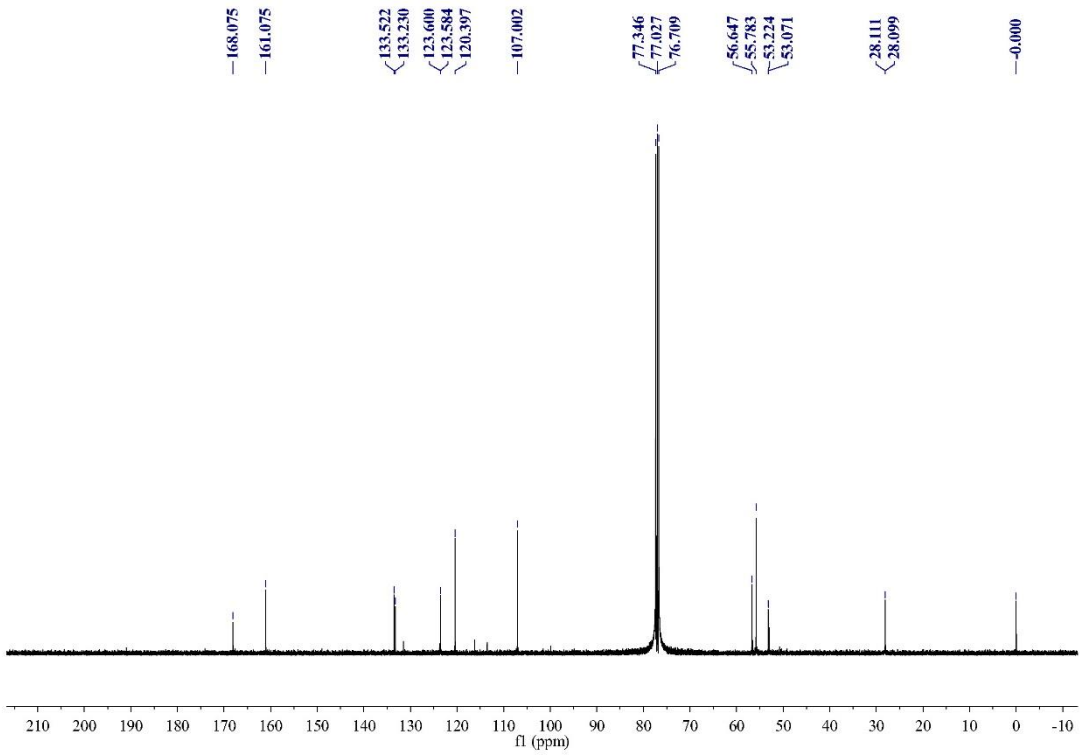
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5d**



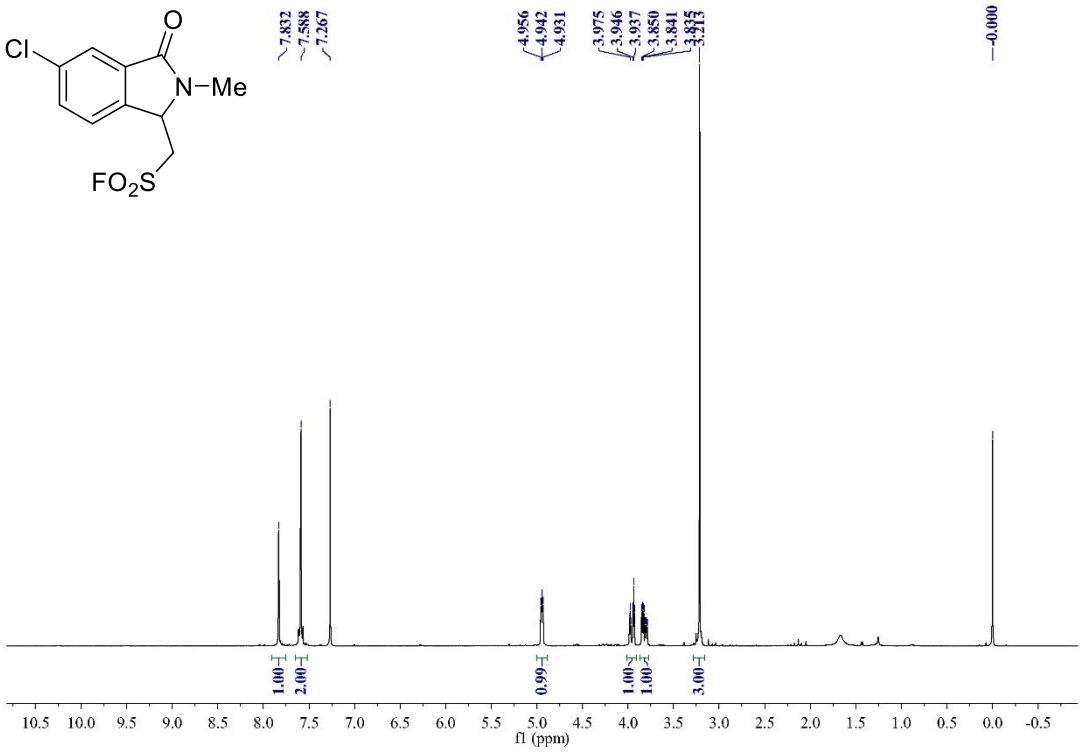
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5d**



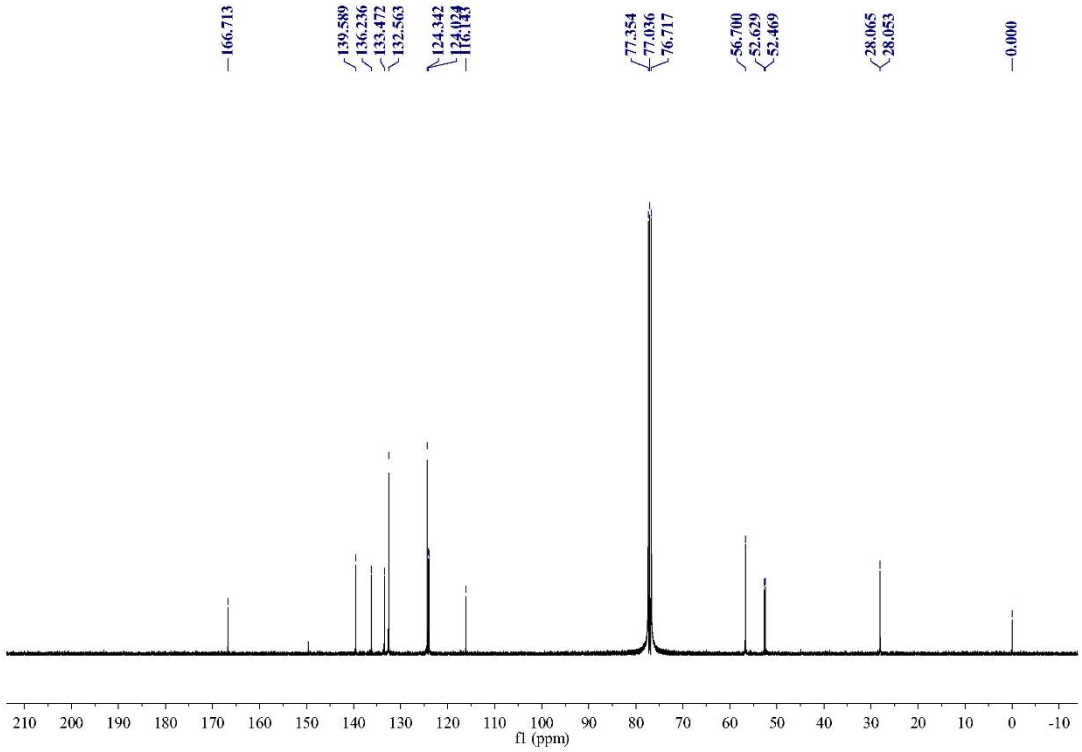
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5e/5e'**



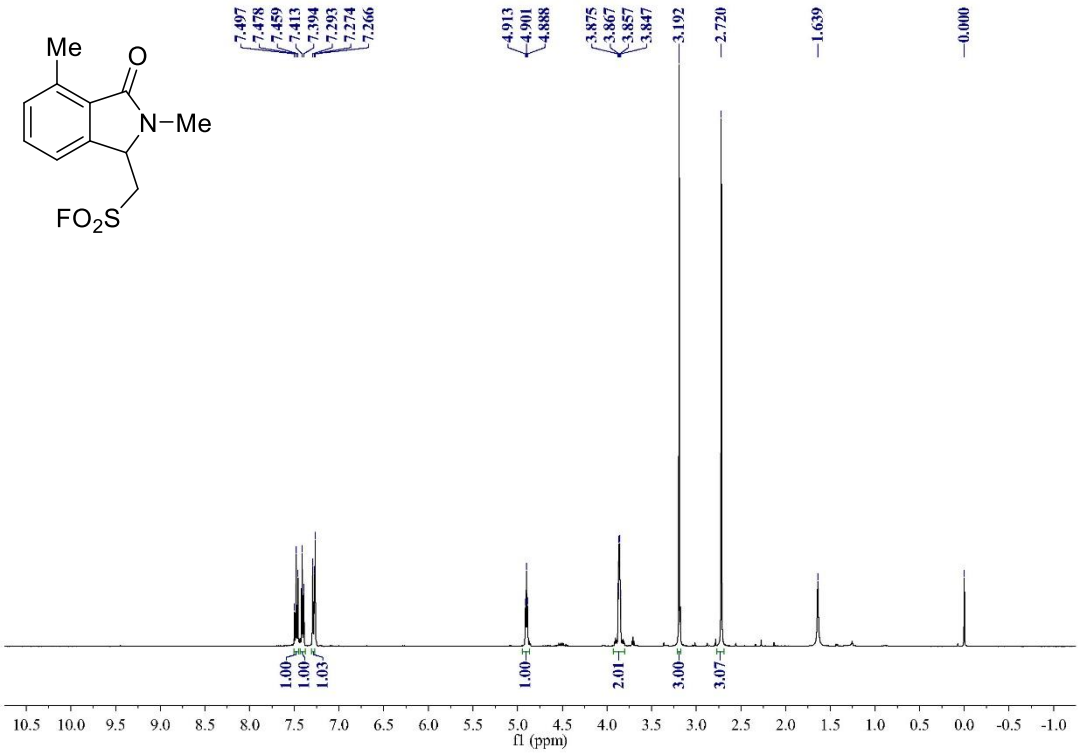
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5e/5e'**



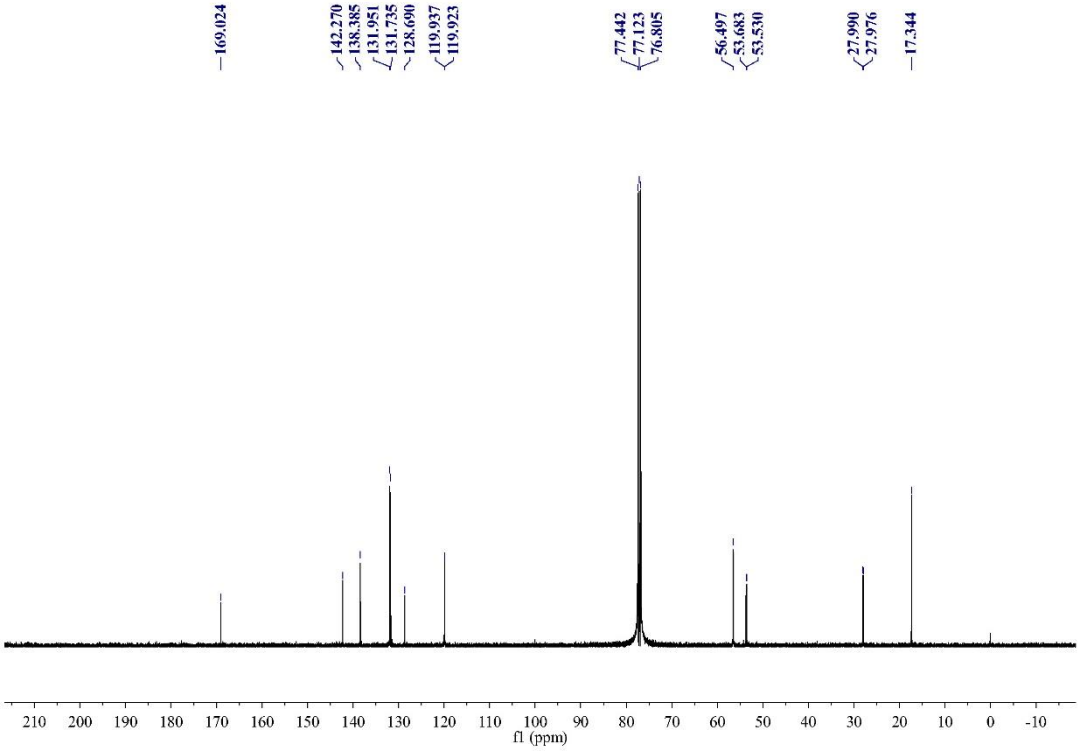
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5f**



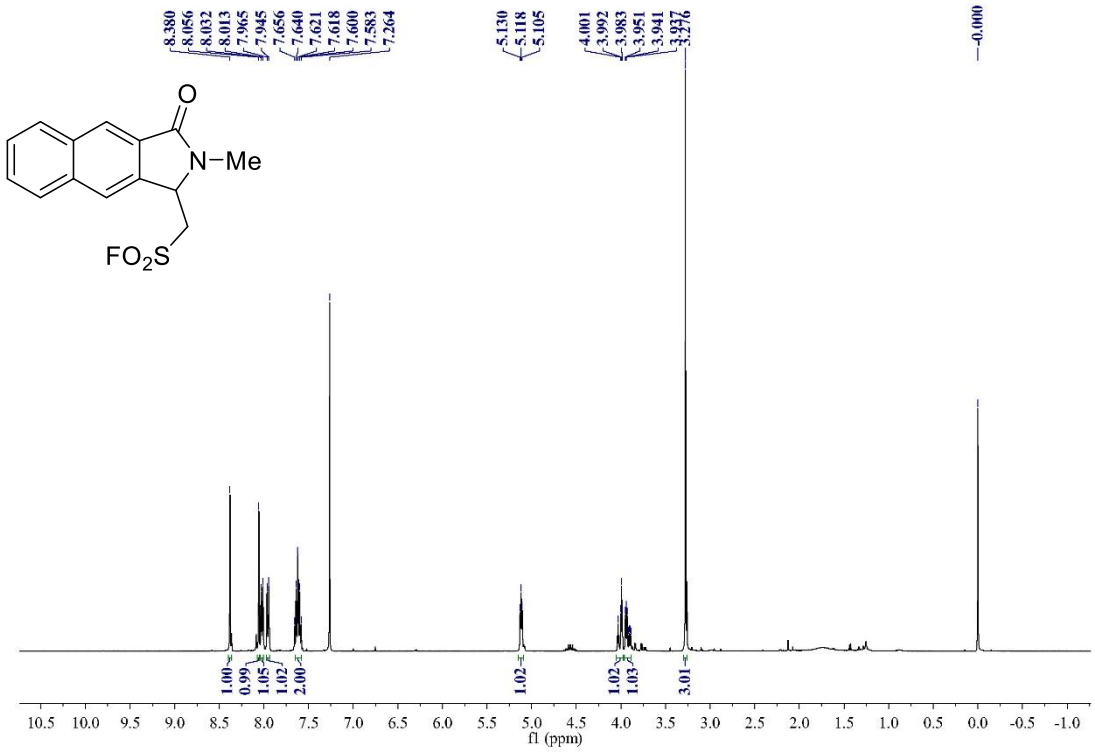
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5f**



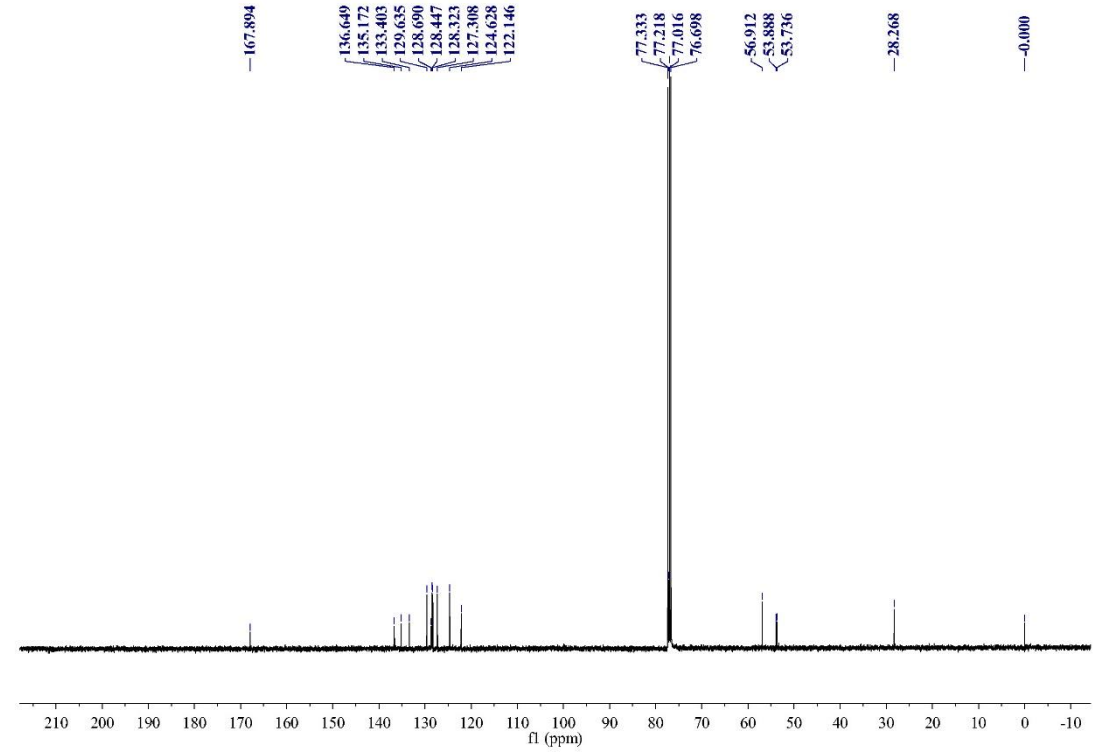
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5g**



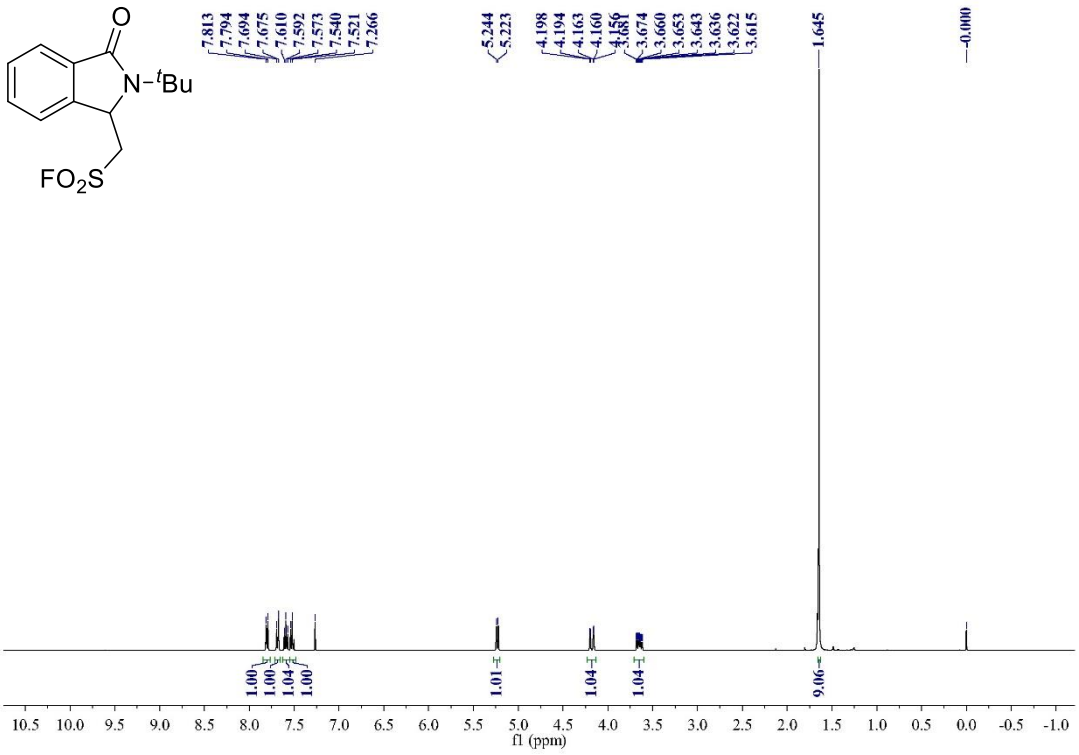
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5g**



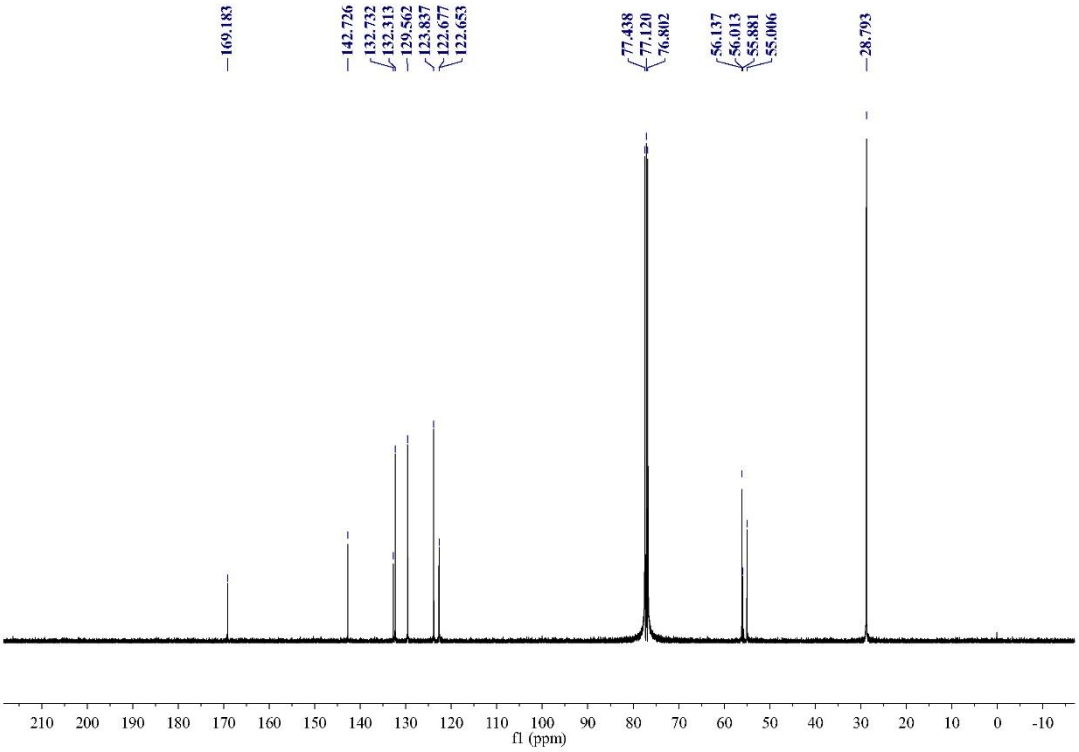
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5h**



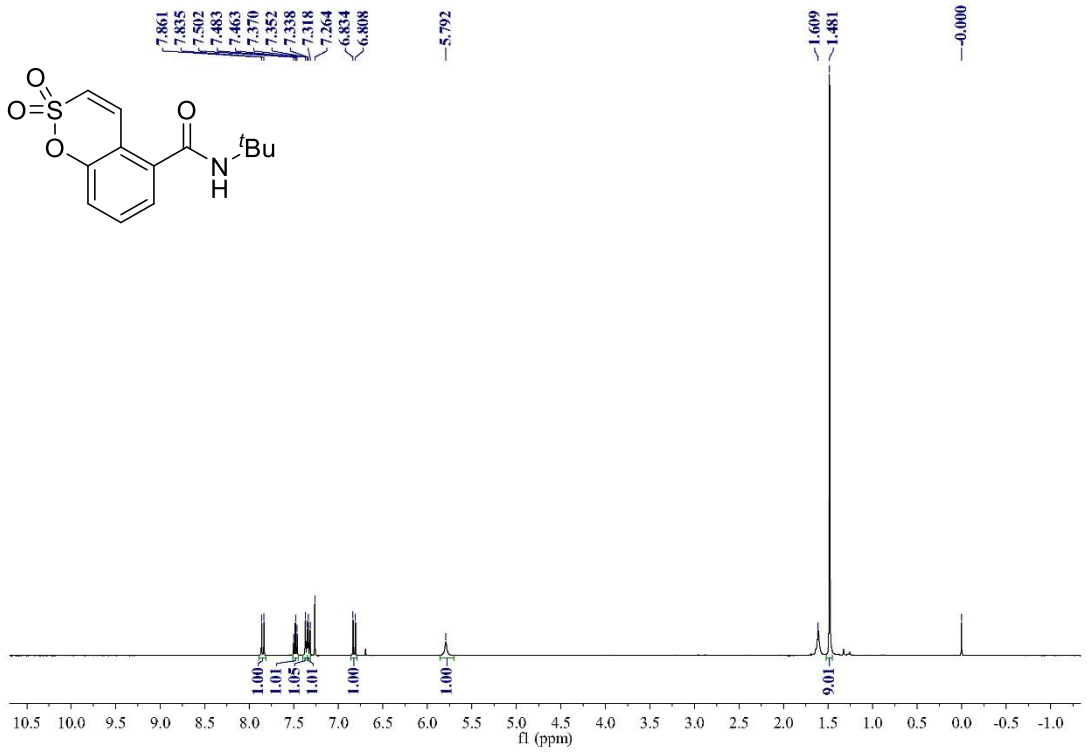
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5h**



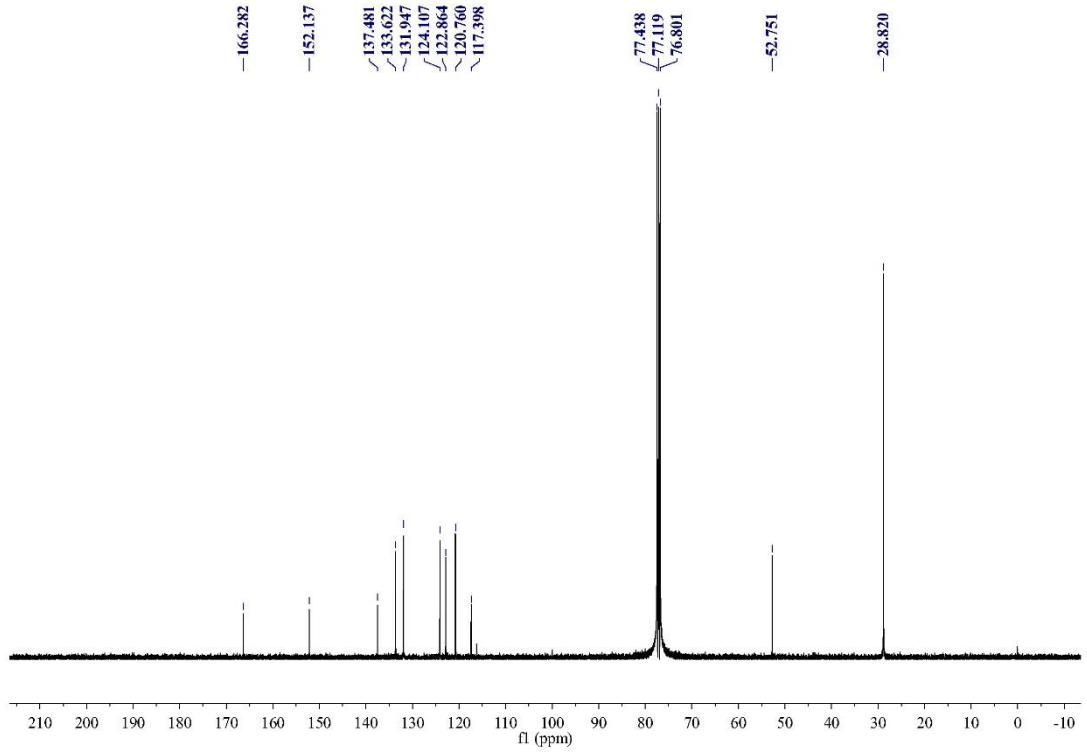
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **6**



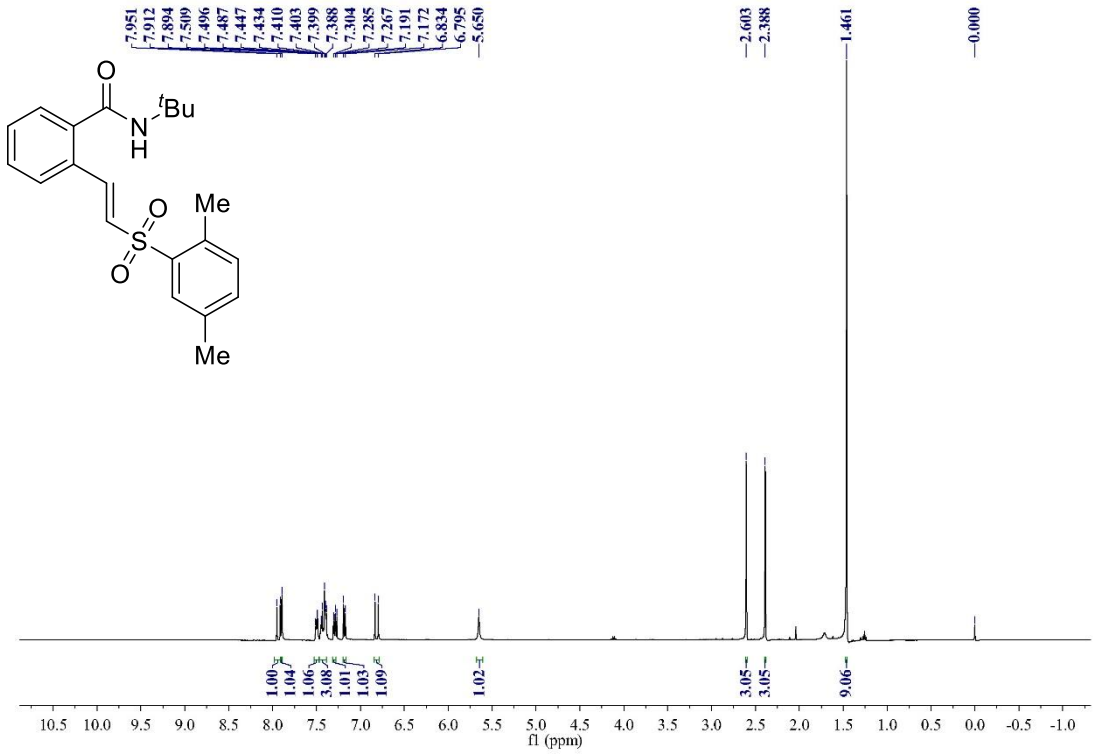
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **6**



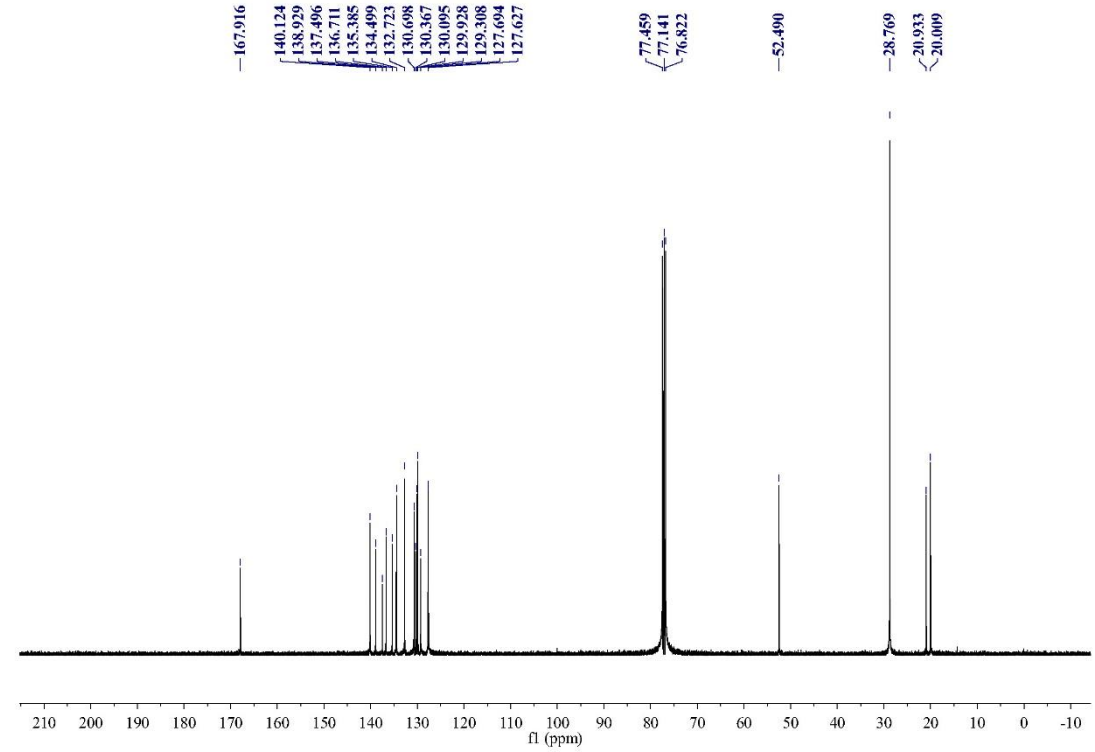
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **7**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **7**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **8**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **8**

Crystal Structure of Compound 3a

Single crystal of **3a** suitable for X-ray crystallography was obtained from dichloromethane by slow evaporation under room temperature under air. The crystal data was collected on an Agilent Gemini E diffractometer (Mo, 50kV 40Ma) and reduced by CrysAlisPro (Rigaku). The structures were solved by direct methods using SHELXS-97. Refinements were performed with SHELXL-2013 using fullmatrix least-squares calculations on F2, with anisotropic displacement parameters for all the nonhydrogen atoms. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2169397.

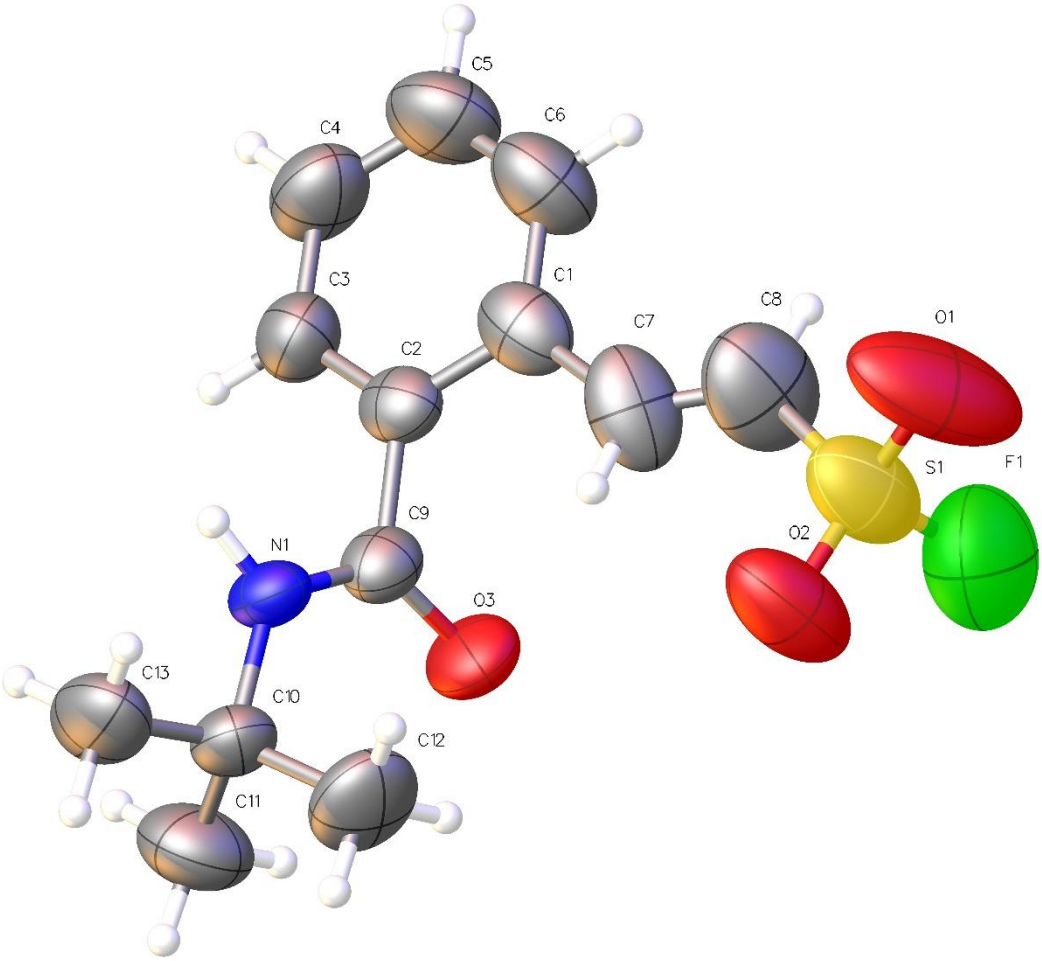


Figure S3. Crystal Structure of **3a** (35% probability level for the thermal ellipsoids)

Table S2. Crystal Data for Compound **3a**

Formula	$C_{13}H_{16}FNO_3S$
Formula weight	285.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.7846 (12) Å, α = 90 deg.
	b = 16.6680 (18) Å, β = 98.592 (11) deg.
	c = 16.942 (2) Å, γ = 90 deg.
Volume	3011.3(6)
Z	8
Density (calculated)	1.259 g / cm^3
Absorption coefficient	0.228 mm^{-1}
F(000)	1200.0
Crystal	0.21 × 0.14 × 0.12 mm
Theta range for data collection	3.82 to 49 deg
Limiting indices	$-10 \le h \le 12$, $-18 \le k \le 19$, $-19 \le l \le 19$
Reflections collected	13084
Independent reflections	5015 [R_{int} = 0.0362, R_{sigma} = 0.0514]
Data / restraints / parameters	5015/3/349
Goodness-of-fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0715, wR_2 = 0.1632
R indices (all data)	R_1 = 0.1330, wR_2 = 0.1998
Largest diff. peak and hole	0.38 and -0.34 e. $Å^{-3}$