Supporting Information

Highly regioselective C–H carbonylation of alkenes with phenyl formate *via* aryl to vinyl 1,4-palladium migration

Tao Ye,[a,b] Fangyuan Cheng,[a] Jian Zhang,[a] Yang-Zi Liu,[a] Quannan Wang,*[a] and Wei-Ping Deng*[a,b]

[a]*Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Department of Chemistry, Zhejiang Normal University, 688 Yingbin Road, Jinhua 321004, P. R. China.*

[b] *Shanghai Frontiers Science Center of Optogenetic Techniques for Cell Metabolism, School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China.*

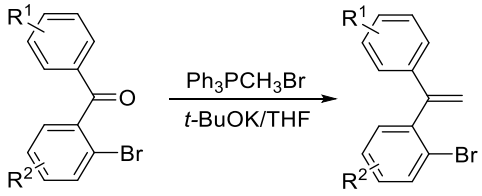
E-mail: wqn1991@zjnu.edu.cn, dengwp827@zjnu.edu.cn.

Contents

1. General information

^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, brs = broad singlet, coupling constant (s) *J* are reported in Hz and relative integrations are reported. ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal chloroform signal at 77.16 ppm as a standard. Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier mass spectrometer using EI-TOF (electron ionization-time of flight) or on a JEOC AccuTOF LC-plus 4G mass spectrometer using ESI (electrospray ionization).

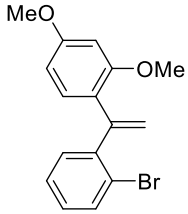
2. Synthesis and characterization data of alkene substrates 1



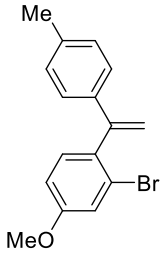
S1 **1**

Substrates **1** were synthesized according to the literature procedure **A**.[1] Spectral data of most compounds was in accordance with those reported in the literature.

General procedure A: To the solution of methyl triphenylphosphonium bromide (7.2 mmol) in 25 mL THF was added *t*-BuOK (10.8 mmol) at ambient temperature. After stirred for 30 min under N_2, the solution of ketone **S1** (3.6 mmol) in 15 mL THF was added slowly and the resulting mixture was further stirred at ambient temperature for 4 h. The reaction was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford product **1**.

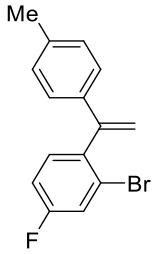


1-(1-(2-Bromophenyl)vinyl)-2,4-dimethoxybenzene (1f) Following the general procedure A, compound **1f** was obtained as a white solid in 87% yield (1.0 g); m.p. 31-32 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.22 (m, 2H), 7.16 – 7.05 (m, 1H), 6.84 – 6.68 (m, 3H), 5.83 (s, 1H), 5.45 (s, 1H), 3.73 (s, 3H), 3.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 151.7, 146.3, 143.7, 132.9, 131.3, 131.2, 128.5, 127.0, 122.6, 120.6, 116.9, 113.3, 113.2, 56.6, 55.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{16}H_{16}BrO_2$ $[M+H]^+$: 319.0334, found: 319.0325.



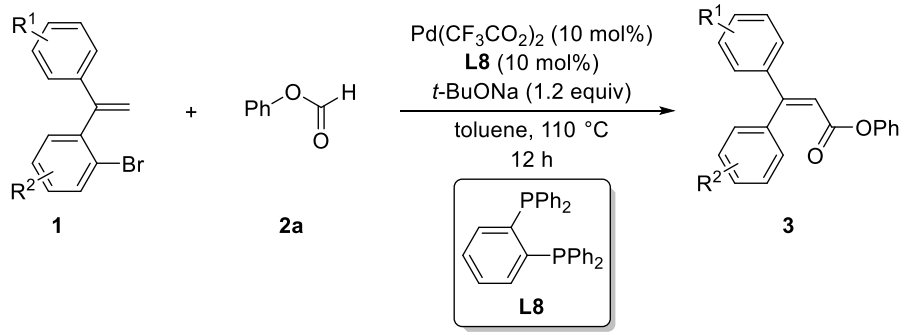
2-Bromo-4-methoxy-1-(1-(*p*-tolyl)vinyl)benzene (1u): Following the general procedure A, compound **1u** was obtained as a white solid in 93% yield (1.0 g); m.p. 76-77 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.12 (m, 4H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.90 – 6.84 (m, 1H), 5.75

(s, 1H), 5.18 (s, 1H), 3.81 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 148.5, 137.6, 137.3, 135.3, 132.1, 129.1 (2C), 126.6 (2C), 123.7, 118.2, 115.3, 113.4, 55.7, 21.3; **HRMS** (ESI-TOF, m/z): calcd for $C_{16}H_{16}BrO$ $[M+H]^+$: 303.0385, found: 303.0387.

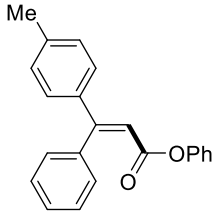


2-Bromo-4-fluoro-1-(1-(*p*-tolyl)vinyl)benzene (1v): Following the general procedure A, compound **1v** was obtained as a colorless oil in 91% yield (0.95 g); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.26 (dd, *J* = 8.5, 6.1 Hz, 1H), 7.16 – 7.08 (m, 4H), 7.07 – 7.01 (m, 1H), 5.79 (s, 1H), 5.18 (s, 1H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8 (d, CF, $^1J_{C\text{-}F}$ = 250.4 Hz), 148.0, 139.1 (d, CF, $^4J_{C\text{-}F}$ = 3.6 Hz), 137.9, 136.7, 132.4 (d, CF, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.2(2C), 126.5(2C), 123.6 (d, CF, $^3J_{C\text{-}F}$ = 9.6 Hz), 120.2 (d, CF, $^2J_{C\text{-}F}$ = 24.2 Hz), 115.7, 114.5 (d, CF, $^2J_{C\text{-}F}$ = 20.9 Hz), 21.3; **HRMS** (ESI-TOF, m/z): calcd for $C_{15}H_{13}BrF$ $[M+H]^+$: 291.0185, found: 291.0170.

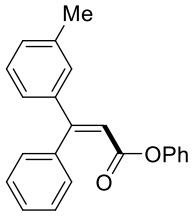
3. General procedure for the synthesis of products 3



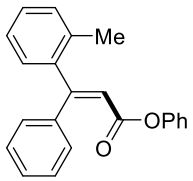
General procedure B: Under a nitrogen atmosphere a mixture of alkene **1** (0.3 mmol, 1.0 equiv), phenyl formate (**2a**) (0.6 mmol, 2.0 equiv), $Pd(CF_3CO_2)_2$ (10 mg, 0.03 mmol, 10 mol%), **L8** (14 mg, 0.03 mmol, 10 mol%), and *t*-BuONa (34.6 mg, 0.36 mmol, 1.2 equiv) in 3.0 mL toluene was stirred at 110 °C for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with 5 mL EtOAc, filtered through a short pad of celite, and washed with 10 mL EtOAc. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to afford **3**.



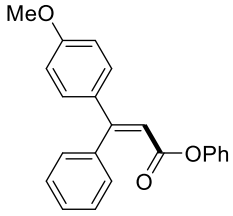
(*E*)-3-Phenyl-3-(*p*-tolyl)acrylate (3a): Following the general procedure B, compound **3a** was obtained as a white solid in 91% yield (86.3 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 128-129 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.38 (m, 3H), 7.30 – 7.23 (m, 6H), 7.18 – 7.12 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 158.9, 150.8, 140.3, 138.9, 137.9, 129.3 (2C), 129.3 (4C), 128.6 (2C), 128.4, 128.1 (2C), 125.6, 121.7 (2C), 115.5, 21.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found: 315.1376.



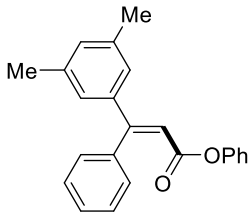
Phenyl (*E*)-3-phenyl-3-(*m*-tolyl)acrylate (3b): Following the general procedure B, compound **3b** was obtained as a white solid in 94% yield (90.5 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 106-107 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 3H), 7.33 – 7.27 (m, 4H), 7.25 – 7.18 (m, 3H), 7.17 – 7.12 (m, 2H), 7.00 – 6.96 (m, 2H), 6.56 (s, 1H), 2.35 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.5, 159.1, 150.7, 140.8, 138.8, 138.3, 130.7, 129.3 (4C), 129.1, 128.5, 128.5, 128.1 (2C), 125.9, 125.6, 121.7 (2C), 116.3, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found: 315.1376.



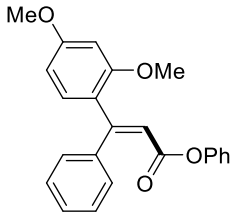
Phenyl (*E*)-3-phenyl-3-(*o*-tolyl)acrylate (3c): Following the general procedure B, compound **3c** was obtained as a white solid in 92% yield (86.8 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 77-78 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 10H), 7.20 – 7.16 (m, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.22 (s, 1H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 159.4, 150.7, 141.9, 138.6, 136.2, 130.9, 129.7, 129.5 (2C), 129.4 (2C), 128.9, 128.8, 128.0 (2C), 125.9, 125.8, 121.7 (2C), 119.1, 20.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found: 315.1376.



Phenyl (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate (3d): Following the general procedure B, compound **3d** was obtained as a white solid in 89% yield (88.2 mg); R_f = 0.3 (petroleum ether/EtOAc = 10/1, v/v); m.p. 131-132 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 3H), 7.34 – 7.26 (m, 5H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.17 – 7.11 (m, 1H), 7.01 – 6.96 (m, 2H), 6.91 – 6.84 (m, 2H), 6.52 (s, 1H), 3.83 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.5, 161.2, 158.7, 150.8, 139.0, 133.0, 130.1 (2C), 129.2(9) (2C), 129.2(5) (2C), 128.4, 128.1 (2C), 125.5, 121.7 (2C), 114.2, 114.0 (2C), 55.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_3$ $[M+H]^+$: 331.1334, found: 331.1327.

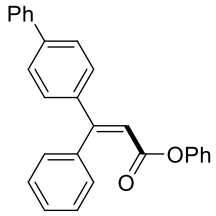


Phenyl (*E*)-3-(3,5-dimethylphenyl)-3-phenylacrylate (3e): Following the general procedure B, compound **3e** was obtained as a white solid in 95% yield (93.6 mg); R_f = 0.6 (petroleum ether/EtOAc = 10/1, v/v); m.p. 127-128 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.3, 1.8 Hz, 3H), 7.33 – 7.25 (m, 4H), 7.17 – 7.12 (m, 1H), 7.03 (s, 1H), 6.98 (d, *J* = 8.7 Hz, 4H), 6.54 (s, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 159.4, 150.8, 140.8, 138.9, 138.1(2C), 131.7, 129.3 (4C), 128.4, 128.0 (2C), 126.5 (2C), 125.6, 121.7 (2C), 116.2, 21.4 (2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1542, found: 329.1533.

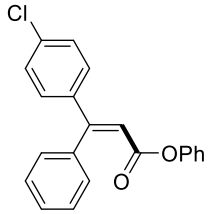


Phenyl (*E*)-3-(2,4-dimethoxyphenyl)-3-phenylacrylate (3f): Following the general procedure B, compound **3f** was obtained as a white solid in 90% yield (97.4 mg); R_f = 0.3 (petroleum ether/EtOAc = 10/1, v/v); m.p. 92-93 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 7H), 7.20 – 7.12 (m, 1H), 7.01 – 6.95 (m, 2H), 6.88 – 6.83 (m, 2H), 6.79 – 6.73 (m, 1H), 6.52 (s, 1H), 3.73 (s, 3H), 3.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 155.9, 153.5, 151.8, 150.7, 139.5, 131.7, 129.3 (2C), 128.9 (2C), 128.2, 127.7 (2C), 125.6, 121.6 (2C), 119.7,

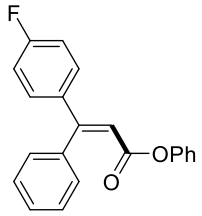
117.1, 115.0, 113.4, 56.5, 55.9; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{21}O_4$ $[M+H]^+$: 361.1440, found: 361.1433.



Phenyl (*E*)-3-([1,1'-biphenyl]-4-yl)-3-phenylacrylate (3g): Following the general procedure B, compound **3g** was obtained as a white solid in 90% yield (101.8 mg); R_f = 0.4 (petroleum ether/EtOAc = 10/1, v/v); m.p. 186-187 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 6.4 Hz, 4H), 7.49 – 7.36 (m, 8H), 7.31 (m, 4H), 7.21 – 7.13 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 158.4, 150.7, 142.8, 140.3, 139.5, 138.7, 129.3 (4C), 129.1 (2C), 129.0 (2C), 128.6, 128.2 (2C), 128.0, 127.3 (2C), 127.2 (2C), 125.7, 121.7 (2C), 116.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}O_2$ $[M+H]^+$: 377.1542, found: 377.1534.

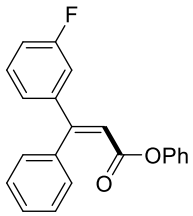


Phenyl (*E*)-3-(4-chlorophenyl)-3-phenylacrylate (3h): Following the general procedure B, compound **3h** was obtained as a white solid in 92% yield (92.4 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 86-87 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.35 – 7.29 (m, 6H), 7.28 – 7.25 (m, 2H), 7.16 (m, 1H), 7.00 – 6.94 (m, 2H), 6.55 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 157.5, 150.6, 139.2, 138.3, 136.1, 129.9 (2C), 129.4 (2C), 129.3 (2C), 128.9 (2C), 128.8, 128.3 (2C), 125.7, 121.6 (2C), 116.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{16}ClO_2$ $[M+H]^+$: 335.0839, found: 335.0832.

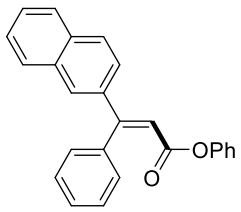


Phenyl (*E*)-3-(4-fluorophenyl)-3-phenylacrylate (3i): Following the general procedure B, compound **3i** was obtained as a white solid in 93% yield (88.8 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 70-71 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.3, 1.7 Hz, 3H), 7.37 – 7.32 (m, 3H), 7.29 – 7.24 (m, 3H), 7.19 – 7.13 (m, 1H), 7.07 – 7.02 (m, *J* = 8.6

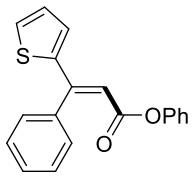
Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 163.9 (d, CF, $^1J_{C\text{-}F}$ = 250.8 Hz), 157.7, 150.7, 138.5, 136.9 (d, CF, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.5 (d, CF, $^3J_{C\text{-}F}$ = 8.5 Hz) (2C), 129.4 (2C), 129.3 (2C), 128.7, 128.2 (2C), 125.7, 121.6 (2C), 116.3 (d, *J* = 1.6 Hz), 115.7 (d, CF, $^2J_{C\text{-}F}$ = 21.8 Hz) (2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{16}FO_2$ $[M+H]^+$: 319.1134, found: 319.1130.



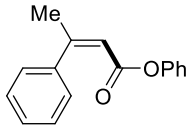
Phenyl (*E*)-3-(3-fluorophenyl)-3-phenylacrylate (3j): Following the general procedure B, compound **3j** was obtained as a white solid in 92% yield (88.1 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 124-125 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 3H), 7.35 – 7.29 (m, 3H), 7.28 – 7.26 (m, 2H), 7.18 – 7.14 (m, 2H), 7.11 – 7.07 (m, 1H), 7.06 – 7.03 (m, 1H), 6.99 – 6.96 (m, 2H), 6.57 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.2, 162.8 (d, CF, $^1J_{C\text{-}F}$ = 246.8 Hz), 157.3, 150.6, 143.0 (d, CF, $^3J_{C\text{-}F}$ = 7.3 Hz), 138.1, 130.1 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.4(2C), 129.3 (2C), 128.8, 128.3 (2C), 125.8, 124.2 (d, CF, $^4J_{C\text{-}F}$ = 2.8 Hz), 121.6 (2C), 117.5, 116.8 (d, CF, $^2J_{C\text{-}F}$ = 21.1 Hz), 115.5 (d, CF, $^2J_{C\text{-}F}$ = 22.6 Hz); **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{16}FO_2$ $[M+H]^+$: 319.1134, found: 319.1128.



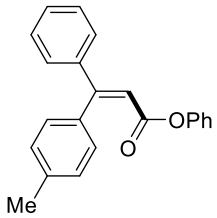
Phenyl (*E*)-3-(naphthalen-2-yl)-3-phenylacrylate (3k): Following the general procedure B, compound **3k** was obtained as a white solid in 93% yield (97.7 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 160-161 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.80 – 7.77 (m, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.56 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.50 – 7.47 (m, 1H), 7.42 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.36 – 7.30 (m, 4H), 7.19 – 7.14 (m, 1H), 7.03 – 6.99 (m, 2H), 6.72 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 158.8, 150.8, 138.7, 138.0, 134.0, 133.1, 129.5 (2C), 129.4 (2C), 129.3, 128.9, 128.6, 128.3, 128.2 (2C), 127.8, 127.3, 126.7, 125.7, 125.3, 121.7 (2C), 116.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{19}O_2$ $[M+H]^+$: 351.1385, found: 351.1377.



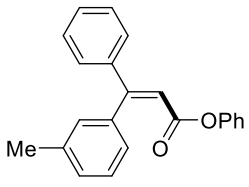
Phenyl (*E*)-3-phenyl-3-(thiophen-2-yl)acrylate (3l): Following the general procedure B, compound **3l** was obtained as a white solid in 65% yield (60 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 88-89 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 4H), 7.35 – 7.32 (m, 2H), 7.29 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.01 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.99 – 6.97 (m, 2H), 6.92 (dd, *J* = 3.8, 1.1 Hz, 1H), 6.61 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 152.3, 150.7, 144.9, 137.9, 130.9, 129.3 (2C), 129.0, 128.8 (2C), 128.6, 128.2, 128.1 (2C), 125.6, 121.7 (2C), 113.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{19}H_{15}O_2S$ $[M+H]^+$: 307.0793, found: 307.0784.



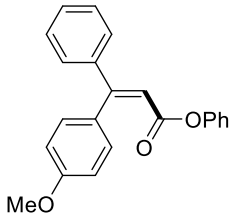
Phenyl (*Z*)-3-phenylbut-2-enoate (3m): Following the general procedure B, compound **3m** was obtained as a colorless oil in 60% yield (43 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 7H), 7.17 – 7.08 (m, 1H), 6.94 (dd, *J* = 8.6, 1.2 Hz, 2H), 6.13 (d, *J* = 1.5 Hz, 1H), 2.26 (d, *J* = 1.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 158.2, 150.7, 140.5, 129.3 (2C), 128.1(7), 128.1(5) (2C), 127.0 (2C), 125.6, 121.6 (2C), 117.0, 27.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{16}H_{15}O_2$ $[M+H]^+$: 239.1072, found: 239.1063.



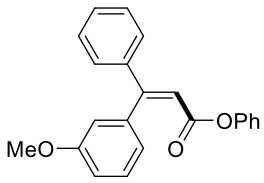
Phenyl (*Z*)-3-phenyl-3-(*p*-tolyl)acrylate (3n): Following the general procedure B, compound **3n** was obtained as a white solid in 91% yield (86 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1 v/v); m.p. 105-106 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 5H), 7.33 – 7.28 (m, 2H), 7.17 (d, *J* = 9.7 Hz, 5H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 159.3, 150.8, 141.1, 138.5, 135.7, 129.8, 129.4(2C), 129.3(2C), 128.8(2C), 128.7(2C), 128.5(2C), 125.6, 121.7(2C), 116.1, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found: 315.1376.



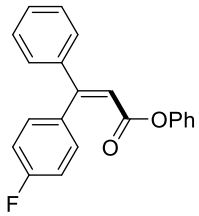
Phenyl (*Z*)-3-phenyl-3-(m-tolyl)acrylate (3o): Following the general procedure B, compound **3o** was obtained as a white solid in 83% yield (78.2 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 98-99 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 5H), 7.34 – 7.26 (m, 3H), 7.19 – 7.12 (m, 2H), 7.11 – 7.05 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.54 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 159.0, 150.8, 140.9, 138.7, 137.7, 129.8(4), 129.8(2), 129.3, 129.3, 129.3, 128.5(7) (2C), 128.6 (2C), 128.0, 126.5, 125.6, 121.6 (2C), 116.4, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1385, found: 315.1377.



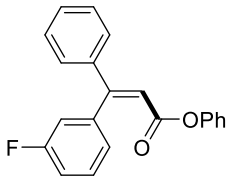
Phenyl (*Z*)-3-(4-methoxyphenyl)-3-phenylacrylate (3p): Following the general procedure B, compound **3p** was obtained as a white solid in 92% yield (91.2 mg); R_f = 0.3 (petroleum ether/EtOAc = 10/1, v/v); m.p. 106-107 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 7H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.48 (s, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 160.1, 159.2, 150.8, 141.5, 131.3 (2C), 130.7, 129.9, 129.4 (2C), 128.9 (2C), 128.5 (2C), 125.6, 121.8 (2C), 115.7, 113.5 (2C), 55.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_3$ $[M+H]^+$: 331.1334, found: 331.1327.



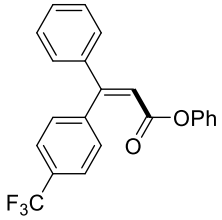
Phenyl (*Z*)-3-(3-methoxyphenyl)-3-phenylacrylate (3q): Following the general procedure B, compound **3q** was obtained as a white solid in 85% yield (84.3 mg); R_f = 0.4 (petroleum ether/EtOAc = 10/1, v/v); m.p. 74-75 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 5H), 7.33 – 7.27 (m, 3H), 7.19 – 7.13 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.83 – 6.76 (m, 1H), 6.56 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 159.4, 158.4, 150.7, 140.4, 140.1, 129.9, 129.3 (2C), 129.2, 128.6 (2C), 128.5 (2C), 125.7, 121.8, 121.6 (2C), 116.5, 114.9, 114.0, 55.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{19}O_3$ $[M+H]^+$: 331.1334, found: 331.1326.



Phenyl (*Z*)-3-(4-fluorophenyl)-3-phenylacrylate (3r): Following the general procedure B, compound **3r** was obtained as a white solid in 89% yield (85 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 122-123 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.37 – 7.29 (m, 6H), 7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 1H), 7.11 – 7.04 (m, 2H), 7.03 – 7.00 (m, 2H), 6.57 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 163.0 (d, CF, $^1J_{C\text{-}F}$ = 248.0 Hz), 158.1, 150.6, 140.7, 134.4 (d, CF, $^4J_{C\text{-}F}$ = 3.5 Hz), 131.3 (d, CF, $^3J_{C\text{-}F}$ = 8.1 Hz) (2C), 130.1, 129.4 (2C), 128.7 (2C), 128.6 (2C), 125.8, 121.6 (2C), 116.6, 115.2 (d, CF, $^2J_{C\text{-}F}$ = 21.7 Hz) (2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{16}FO_2$ $[M+H]^+$: 319.1134, found: 319.1128.

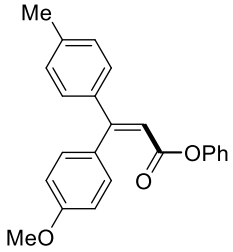


Phenyl (*Z*)-3-(3-fluorophenyl)-3-phenylacrylate (3s): Following the general procedure B, compound **3s** was obtained as a white solid in 91% yield (87 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 85-86 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 1H), 7.37 (qd, *J* = 7.3, 6.8, 1.9 Hz, 5H), 7.32 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.09 – 7.05 (m, 2H), 7.02 – 6.97 (m, 3H), 6.60 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.1, 162.6 (d, CF, $^1J_{C\text{-}F}$ = 246.4 Hz), 157.4, 150.6, 140.8 (d, CF, $^3J_{C\text{-}F}$ = 7.8 Hz), 140.0, 130.2, 129.7 (d, CF, $^3J_{C\text{-}F}$ = 8.3 Hz), 129.4 (2C), 128.7 (2C), 128.5 (2C), 125.8, 125.0 (d, CF, $^4J_{C\text{-}F}$ = 2.9 Hz), 121.6 (2C), 116.9, 116.3 (d, CF, $^2J_{C\text{-}F}$ = 22.1 Hz), 115.4 (d, CF, $^2J_{C\text{-}F}$ = 21.0 Hz); **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{16}FO_2$ $[M+H]^+$: 319.1134, found: 319.1128.

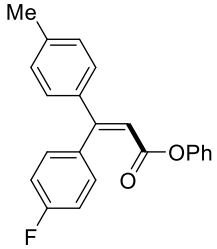


Phenyl (*Z*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)acrylate (3t): Following the general procedure B, compound **3t** was obtained as a white solid in 91% yield (105.5 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 146-147 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.41 (m, 1H), 7.41 – 7.36 (m, 4H), 7.35 – 7.30 (m, 4H), 7.21 – 7.15 (m, 1H), 7.02 – 6.98 (m, 2H), 6.67 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.9, 157.6, 150.4, 142.3, 139.7,

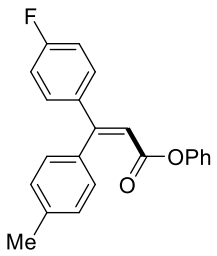
130.3 (q, CF, $^{2}J_{C\text{-}F}$ = 30.5 Hz), 130.2, 129.5 (2C), 129.4 (2C), 128.7 (2C), 128.3 (2C), 125.8, 125.1 (q, CF, $^{3}J_{C\text{-}F}$ = 3.8 Hz) (2C), 124.1 (q, CF, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 121.4 (2C), 117.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{16}F_3O_2$ $[M+H]^+$: 369.1102, found: 369.1098.



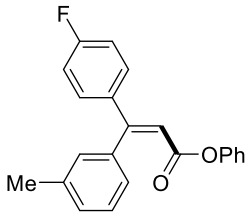
Phenyl (*Z*)-3-(4-methoxyphenyl)-3-(*p*-tolyl)acrylate (3u): Following the general procedure B, compound **3u** was obtained as a white solid in 89% yield (84.3 mg); R_f = 0.3 (petroleum ether/EtOAc = 10/1, v/v); m.p. 158-159 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.20 (m, 4H), 7.19 – 7.12 (m, 3H), 7.08 – 7.00 (m, 2H), 6.94 – 6.85 (m, 2H), 6.46 (s, 1H), 3.81 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.7, 160.0, 159.3, 150.8, 140.2, 138.6, 131.2 (2C), 130.9, 129.3(3) (2C), 129.2(7) (2C), 128.9 (2C), 125.6, 121.8 (2C), 114.8, 113.4 (2C), 55.4, 21.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{21}O_3$ $[M+H]^+$: 345.1491, found: 345.1483.



Phenyl (*Z*)-3-(4-fluorophenyl)-3-(*p*-tolyl)acrylate (3v): Following the general procedure B, compound **3v** was obtained as a white solid in 90% yield (89.8 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 113-114 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.28 – 7.22 (m, 4H), 7.19 – 7.13 (m, 3H), 7.09 – 7.03 (m, 2H), 7.03 – 6.99 (m, 2H), 6.55 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 162.9 (d, CF, $^{1}J_{C\text{-}F}$ = 247.8 Hz), 158.2, 150.7, 140.5, 137.8, 134.6 (d, CF, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 131.3 (d, CF, $^{3}J_{C\text{-}F}$ = 8.2 Hz) (2C), 129.41 (2C), 129.40(2C), 128.6(2C), 125.7, 121.6 (2C), 115.6, 115.1 (d, CF, $^{2}J_{C\text{-}F}$ = 21.6 Hz) (2C), 21.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{18}FO_2$ $[M+H]^+$: 333.1291, found: 333.1282.



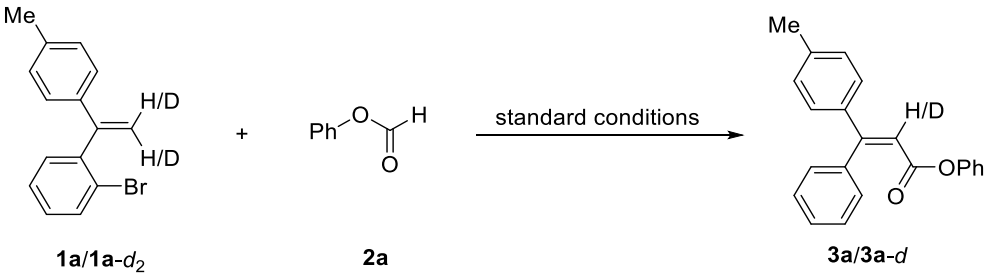
Phenyl (*E*)-3-(4-fluorophenyl)-3-(*p*-tolyl)acrylate (3w): Following the general procedure B, compound **3w** was obtained as a white solid in 95% yield (94.8 mg); R_f = 0.5 (petroleum ether/EtOAc = 10/1, v/v); m.p. 84-85 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 7.17 (q, *J* = 8.1 Hz, 5H), 7.03 (q, *J* = 8.1, 7.6 Hz, 4H), 6.48 (s, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 163.9 (d, $^1J_{C\text{-}F}$ = 250.5 Hz), 158.1, 150.7, 138.8, 137.2 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 135.5, 130.6 (d, CF, $^3J_{C\text{-}F}$ = 8.5 Hz)(2C), 129.4(2C), 129.3(2C), 128.9(2C), 125.7, 121.7(2C), 115.9, 115.6 (d, CF, $^2J_{C\text{-}F}$ = 21.6 Hz)(2C), 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{18}FO_2$ $[M+H]^+$: 333.1291, found: 333.1286.



Phenyl (*Z*)-3-(4-fluorophenyl)-3-(*m*-tolyl)acrylate (3x): Following the general procedure B, compound **3x** was obtained as a white solid in 96% yield (95.8 mg); R_f = 0.6 (petroleum ether/EtOAc = 10/1, v/v); m.p. 68-69 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 7.20 (q, *J* = 7.4 Hz, 2H), 7.13 – 7.05 (m, 4H), 7.03 – 6.98 (m, 2H), 6.53 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 163.8 (d, CF, $^1J_{C\text{-}F}$ = 250.7 Hz), 157.8, 150.7, 138.5, 137.8, 137.0 (d, CF, $^4J_{C\text{-}F}$ = 3.4 Hz), 130.5 (d, CF, $^3J_{C\text{-}F}$ = 8.4 Hz)(2C), 129.8, 129.5, 129.4(2C), 128.1, 126.4, 125.7, 121.6(2C), 116.2 (d, *J* = 1.6 Hz), 115.6 (d, CF, $^2J_{C\text{-}F}$ = 21.7 Hz)(2C), 21.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{18}FO_2$ $[M+H]^+$: 333.1291, found: 333.1284.

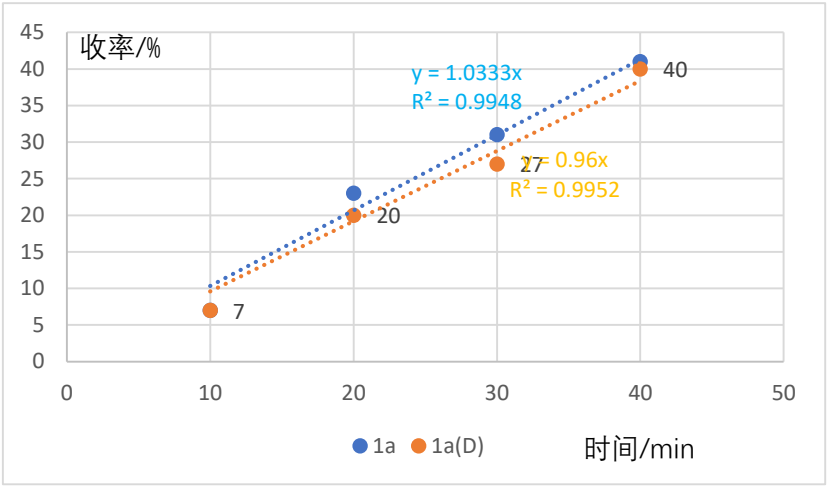
4. The kinetic isotope effect (KIE) experiments

The C–H(D) carbonylation reactions of **1a** and its deuterated form **1a-d_2**, were carried out in a parallel manner under the optimized conditions. The NMR yields from the reactions were carefully checked by the signal integration of the target product **3a** with 1,3,5-trimethoxybenzene as the internal standard. The k_H/k_D value was calculated according to the yields of **3a** and **3a-*d*** from the reactions at time intervals of 10 min, 20 min, 30 min, and 40 min.

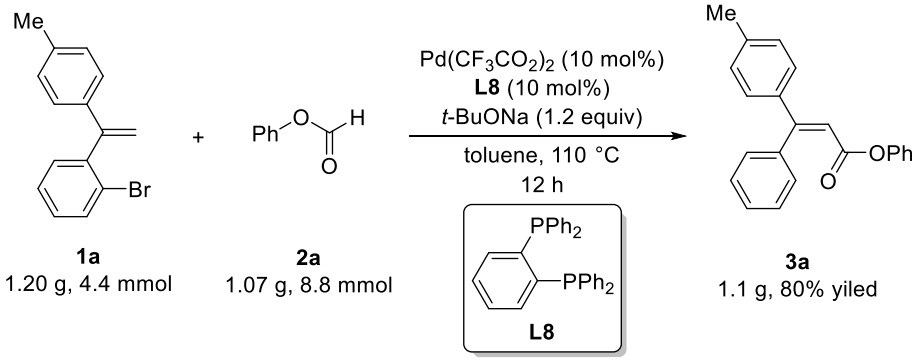


1a/**1a**-d_2 **2a** **3a**/**3a**-*d*

time(min)	10	20	30	40	
1a	7%	23%	31%	41%	
1a-d_2	7%	20%	27%	40%	k_H/k_D = 1.08



5. Gram-scale preparation of compound 3a



1a
1.20 g, 4.4 mmol

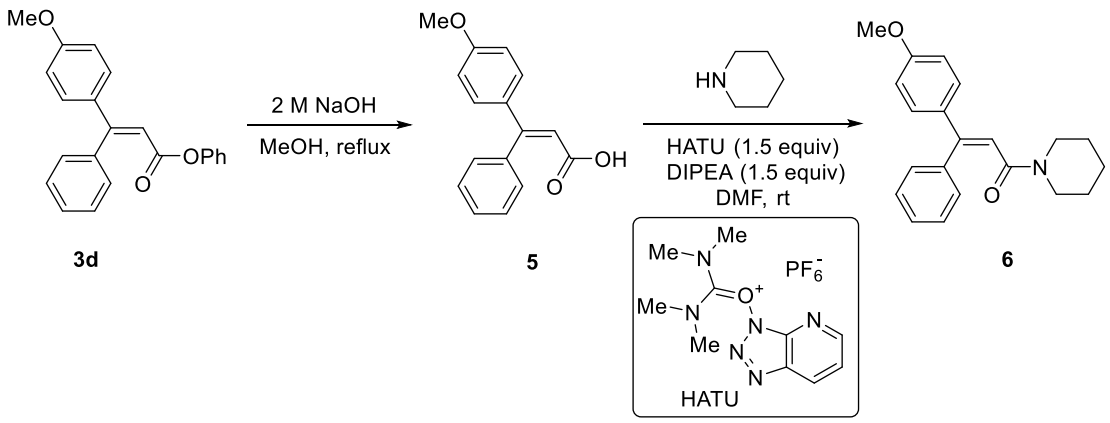
2a
1.07 g, 8.8 mmol

3a
1.1 g, 80% yiled

Under a nitrogen atmosphere a mixture of alkene **1a** (1.2 g, 4.4 mmol), phenyl formate (**2a**) (1.07 g, 8.8 mmol), $Pd(CF_3CO_2)_2$ (146.3 mg, 0.44 mmol), **L8** (205.3 mg, 0.44 mmol), and *t*-BuONa (507.5 mg, 5.28 mmol) in 44 mL toluene was stirred at 110 ºC for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with 30 mL EtOAc, filtered through a short pad of celite, and washed with 60 mL EtOAc. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) to afford **3a** as a white solid

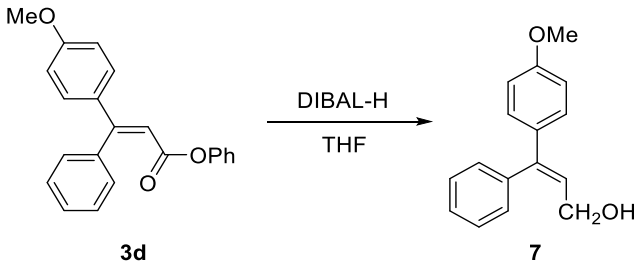
in 80% yield (1.1 g, *E*/*Z* > 20:1).

6. Synthetic transformations



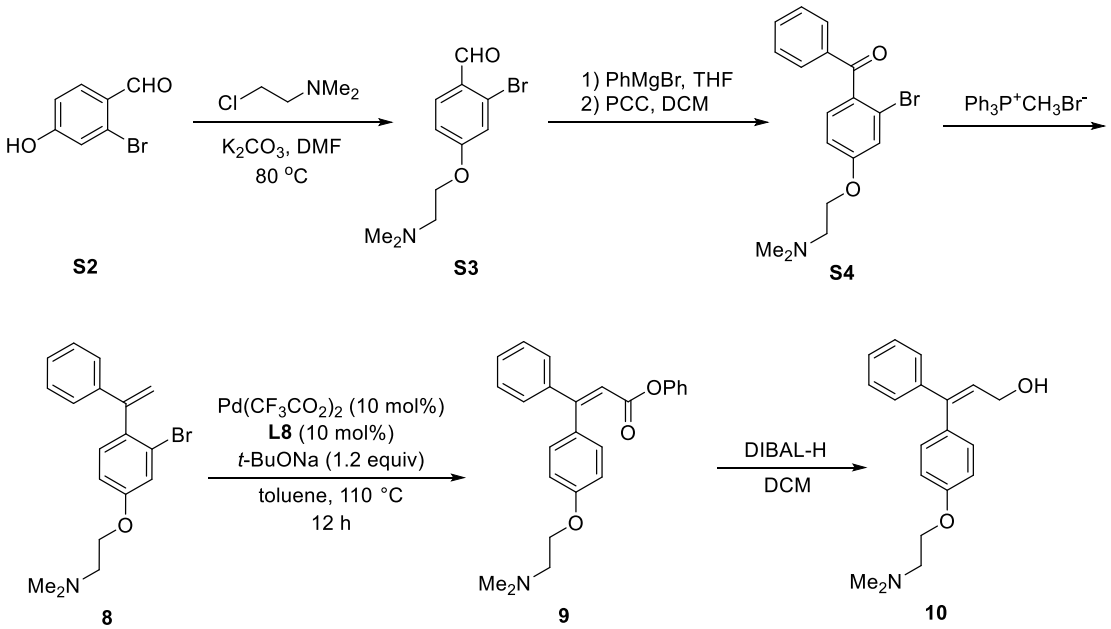
3d (99.2 mg, 0.3 mmol) in 4 mL 2 M NaOH : H_2O (v/v = 3/1) was stirred for 4 h in the air and reflux. The reaction mixture was then cooled to room temperature and added aqueous HCl, adjusted the pH of the solution to 6~7, which filtered and dried to afford the product **6** as a white solid in 92% yield (70.2 mg, *E*/*Z* > 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (m, 3H), 7.24 – 7.17 (m, 4H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.26 (s, 1H), 3.81 (s, 3H).

To a stirred solution of **5** (70 mg, 0.28 mmol) in DMF (0.7 mL) at 0 °C was added 1-[bis(dimethylamino)-methylene]-1*H*-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluoro-phosphate (HATU 159.7 mg, 0.42 mmol) and DIPEA (54.3 mg, 0.42 mmol). The reaction mixture was stirred at room temperature for 1 h, and piperidine (29 mg, 0.34 mmol) was dropwise added. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with H_2O, and extracted with 3 × 5.0 mL EtOAc. The combined organic layers were washed with saturated aqueous NH_4Cl, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v/v) to give the product **6** as a colorless oil in 70% yield (63 mg, *E*/*Z* > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.25 (s, 1H), 3.81 (s, 3H), 3.45 (t, *J* = 5.4 Hz, 2H), 3.22 (t, *J* = 5.6 Hz, 2H), 1.54 – 1.33 (m, 4H), 1.03 (t, *J* = 5.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 159.9, 146.2, 139.2, 133.7, 129.6(2C), 129.4(2C), 128.4, 128.2(2C), 119.9, 113.7(2C), 55.4, 47.4, 42.1, 25.8, 25.2, 24.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1807, found: 322.1798.



3d **7**

3d (99.2 mg, 0.3 mmol) was dissolved in 3 mL DCM and diisobutylaluminum hydride (4.0 equiv, 1 M in hexane) was added at -78 °C, the mixture was stirred for 1 h. 5 mL MeOH and 1 mL 1M HCl was added and the mixture was extracted with DCM. The combined organic layers were dried over Na_2SO_4 and the volatiles were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1, v/v) to give **7** as a pale yellow solid in 83% yield (60 mg, *E*/*Z* > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 3H), 7.17 (m, 4H), 6.87 – 6.76 (m, 2H), 6.17 (t, *J* = 6.9 Hz, 1H), 4.18 (d, *J* = 6.9 Hz, 2H), 3.80 (s, 3H), 1.51 (s, 1H).



2-Bromo-4-hydroxybenzaldehyde **S2** (2.2 g, 10 mmol) in 30 mL DMF was treated with K_2CO_3 (13.2 g, 40 mmol) and heated at 80 °C for 30 min. 2-Dimethylaminoethyl chloride hydrochloride (1729 mg, 6.00 mmol) was added and the mixture was heated at 80° C for 18 h. The mixture was cooled to room temperature and concentrated. The residue was purified by flash column chromatography on silica gel (petroleum ether /EtOAc = 10:1, v/v).

A solution of PhMgBr (11 mmol) in THF was added slowly to a solution of the above aldehyde **S3** (1.5 g, 5.5 mmol) in 20 mL THF at -40 °C under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 2 h and quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc and the combined organic phases were washed

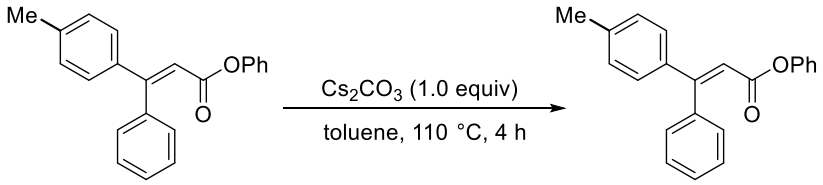
with brine, dried over anhydrous Na_2SO_4. Then, PCC (1.7 g, 7.7 mmol) was added slowly to a solution of the above crude product in 100 mL CH_2Cl_2 at ambient temperature under air. After stirred at rt overnight, the reaction was quenched with the mixture of saturated aqueous Na_2CO_3 solution and saturated aqueous $Na_2S_2O_4$ solution (1:1) and extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (DCM/MeOH = 20:1, v/v). To the solution of methyl triphenylphosphonium bromide (1 g, 2.6 mmol) in 10 mL THF was added *t*-BuOK (450 mg, 3.9 mmol) at ambient temperature. After stirred for 30 min under nitrogen, the solution of the above **S4** (450 mg, 1.3 mmol) in 10 mL THF was added slowly and the resulting mixture was further stirred at ambient temperature for 4 h. The reaction was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (DCM/MeOH = 10/1, v/v) to afford product **8** as a colorless oil in 45% yield (202 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.79 (d, *J* = 1.2 Hz, 1H), 5.24 (d, *J* = 1.2 Hz, 1H), 4.07 (t, *J* = 5.7 Hz, 2H), 2.74 (t, *J* = 5.6 Hz, 2H), 2.35 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 148.6, 140.1, 135.1, 132.1, 128.4 (2C), 127.8, 126.7 (2C), 123.6, 118.8, 116.2, 114.0, 66.4, 58.3, 46.0 (2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{18}H_{21}BrNO$ $[M+H]^+$: 346.0807, found: 346.0792.

Under a nitrogen atmosphere a mixture of alkene **8** (93.2 mg, 0.27 mmol, 1.0 equiv), phenyl formate (**2a**) (66 mg, 0.6 mmol, 2.0 equiv), $Pd(CF_3CO_2)_2$ (9 mg, 0.027 mmol, 10 mol%), **L8** (12.6 mg, 0.027 mmol, 10 mol%), and *t*-BuONa (31.2 mg, 0.324 mmol, 1.2 equiv) in 2.7 mL toluene was stirred at 110 ºC for 12 h. After cooled to ambient temperature, the reaction mixture was diluted with 5 mL EtOAc, filtered through a short pad of celite, and washed with 10 mL EtOAc. The combined filtrate was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (DCM/MeOH = 10/1, v/v) to afford **9** as a white solid in 82% yield (84 mg, *Z*/*E* > 20:1); m.p. 70-71 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 7H), 7.25 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 7.06 – 7.01 (m, 2H), 6.96 – 6.89 (m, 2H), 6.47 (s, 1H), 4.08 (t, *J* = 5.8 Hz, 2H), 2.74 (t, *J* = 5.8 Hz, 2H), 2.34 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 159.4, 159.1, 150.8, 141.5, 131.2 (2C), 130.8, 129.8, 129.4 (2C), 128.9 (2C), 128.5 (2C), 125.6, 121.7 (2C), 115.7, 114.0 (2C), 66.0, 58.4, 46.0 (2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{26}NO_3$ $[M+H]^+$: 388.1913, found: 388.1900.

9 (50 mg, 0.13 mmol) was dissolved in 2 mL DCM and diisobutylaluminum hydride (4.0 equiv, 1 M in hexane) was added at -78 °C, the mixture was stirred for 1 h. 5 mL MeOH and 1

mL 1 M HCl was added and the mixture was extracted with DCM. The combined organic layers were dried over Na_2SO_4 and the volatiles were removed under reduced pressure. The residue was was purified by flash chromatography on silica gel (DCM/MeOH = 10/1, v/v) to give **10** as a white solid in 63% yield (24 mg, *Z*/*E* > 20:1); m.p. 140-141 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.18 (t, *J* = 6.8 Hz, 1H), 4.25 (d, *J* = 6.8 Hz, 2H), 4.11 (t, *J* = 5.7 Hz, 2H), 2.78 (t, *J* = 5.7 Hz, 2H), 2.38 (s, 6H), 1.91 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 144.0, 142.4, 131.6, 131.1 (2C), 128.3 (2C), 127.9 (2C), 127.7, 127.3, 114.3(2C), 65.9, 60.9, 58.3, 46.0 (2C). **HRMS** (ESI-TOF, m/z): calcd for $C_{19}H_{24}NO_2$ $[M+H]^+$: 298.1807, found: 298.1800.

7. Control experiment



3a (*E*/*Z* > 20:1) **3a** (*E*/*Z* > 20:1)

Under a nitrogen atmosphere, **3a** (31 mg, 0.1 mmol, 1.0 equiv) and Cs_2CO_3 (32 mg, 0.1 mmol, 1.0 equiv) in 1 mL toluene was stirred at 110 ºC for 4 h. After cooled to ambient temperature, the reaction mixture was diluted with 5 mL EtOAc, filtered through a short pad of celite, and washed with 10 mL EtOAc. The combined filtrate was concentrated under reduced pressure. The *E*/*Z* ratio of the reaction mixture was determined by crude ^{1}H NMR analysis. Control experiment showed that the *E*/*Z* ratio of **3a** did not decrease in the presence of Cs_2CO_3.

8. X-Ray crystal structures

The corresponding compound **3a** and **3j** (10.0 mg) were dissolved in 1.0 mL dichloromethane. The solution was filtered by millipore filter and transferred to a vial. Then, drops of hexane were added subsequently. A single crystal was obtained by natural volatilization at room temperature. The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with micro-focus Cu radiation source (Kα = 1.54178 Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package.

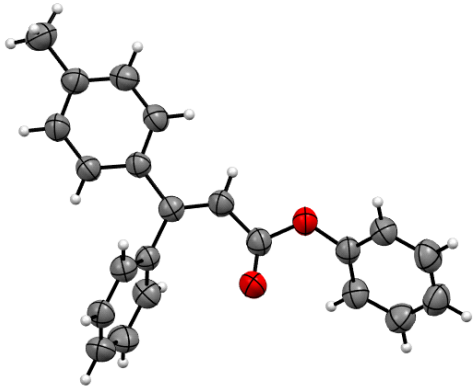


Figure S1 The X-ray crystal structure of **3a** with thermal ellipsoids at the 30% probability level (CCDC: 2235100).

Table S1. Crystal data and structure refinement for 2022101301_0m.

Identification code	2022101301_0m	
Empirical formula	C22 H18 O2	
Formula weight	314.36	
Temperature	273.15 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 5.7762(2) Å	α = 90 °.
	b = 21.0127(8) Å	β = 95.487(3) °.
	c = 14.0970(5) Å	γ = 90 °.
Volume	1703.16(11) $Å^3$	
Z	4	
Density (calculated)	1.226 Mg/m^3	
Absorption coefficient	0.610 mm^{-1}	
F(000)	664	
Crystal size	0.170 x 0.140 x 0.120 mm^3	
Theta range for data collection	3.788 to 68.165 °.	
Index ranges	-6<=h<=6, -25<=k<=24, -16<=l<=11	
Reflections collected	13261	
Independent reflections	2082 [R(int) = 0.0563]	
Completeness to theta = 67.165 °	99.5 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.8145	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3082 / 0 / 219	
Goodness-of-fit on F^2	1.038	

Final R indices [I>2sigma(I)]	R1 = 0.0563, wR2 = 0.1282
R indices (all data)	R1 = 0.0874, wR2 = 0.1511
Extinction coefficient	0.0058(9)
Largest diff. peak and hole	0.198 and -0.149 e.Å^{-3}

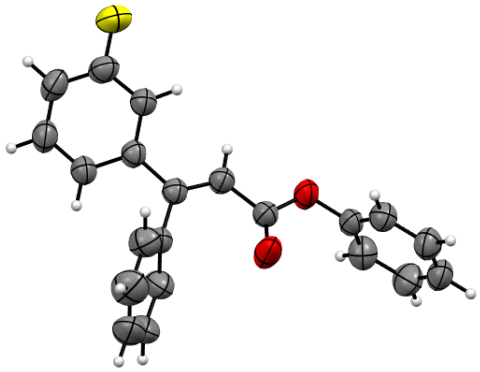


Figure S2 The X-ray crystal structure of **3j** with thermal ellipsoids at the 30% probability level (CCDC: 2235083).

Table S2. Crystal data and structure refinement for cu_g6p_0m_a.

Identification code	cu_g6p_0m_a	
Empirical formula	C21 H15 F O2	
Formula weight	318.33	
Temperature	150 K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 5.7182 (11) Å	α = 90 °.
	b = 18.987 (3) Å	β = 90.241(10) °.
	c = 15.264 (3) Å	γ = 90 °.
Volume	1657.2 (5) Å^3	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.725 mm^{-1}	
F(000)	664	
Crystal size	0.100 x 0.200 x 0.100 mm^3	
Theta range for data collection	3.715 to 68.362 °.	
Index ranges	-6<=h<=6, -19<=k<=22, -17<=l<=18	
Reflections collected	4078	
Independent reflections	2484 [R(int) = 0.0450]	
Completeness to theta = 68.362 °	96.9 %	

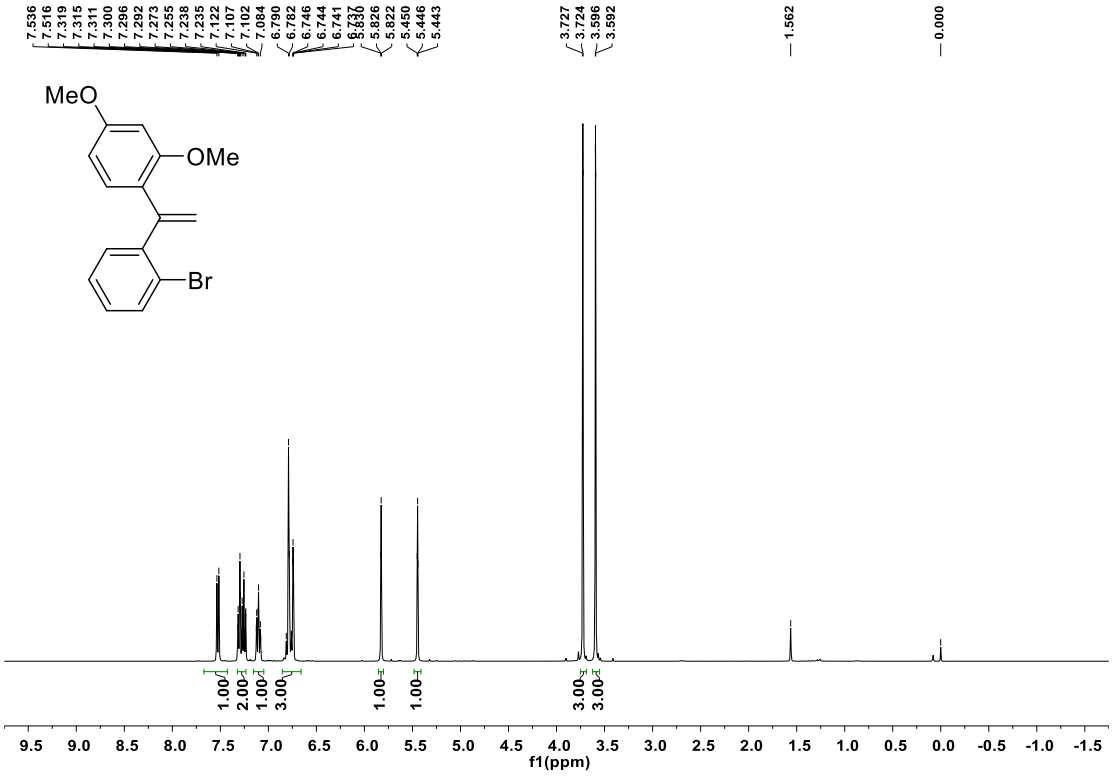
Absorption correction	multi-scan
Max. and min. transmission	0.8806
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2944 / 0 / 217
Goodness-of-fit on F2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1311
R indices (all data)	R1 = 0.0520, wR2 = 0.1383
Extinction coefficient	0.0058(9)
Largest diff. peak and hole	0.266 and -0.281e.$Å^{-3}$

9. References

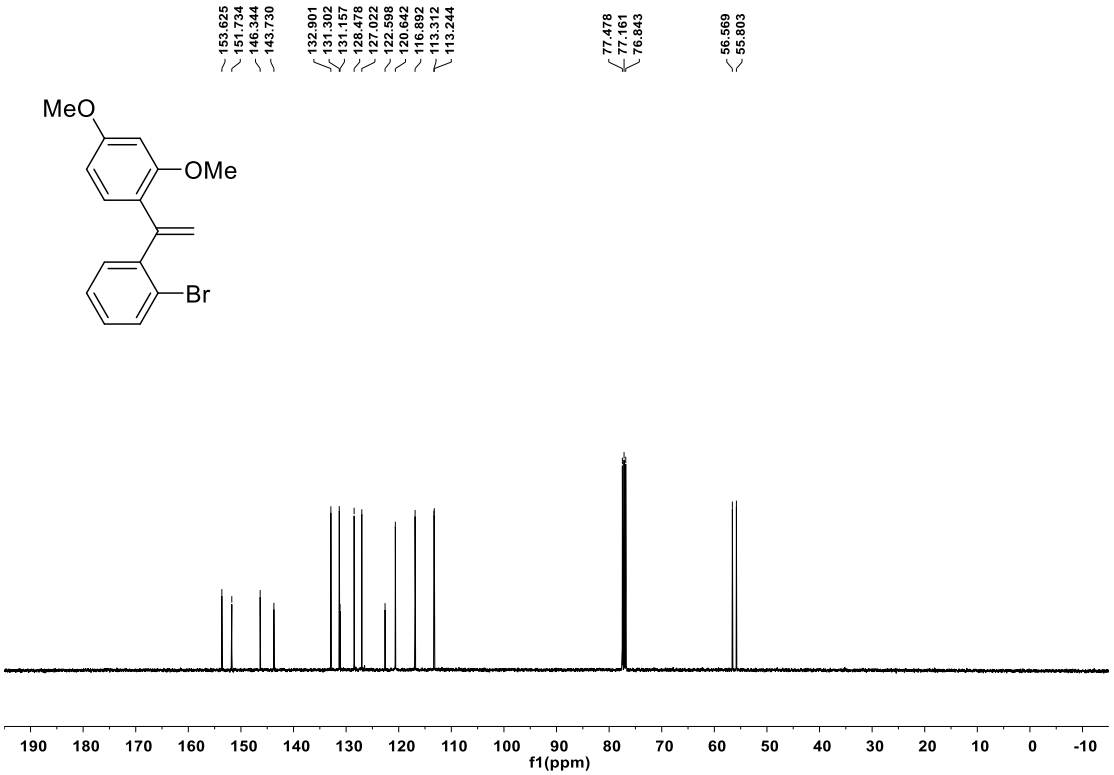
1 (*a*) T.-J. Hu, G. Zhang, Y.-H. Chen, C.-G. Feng and G.-Q. Lin, Borylation of olefin C−H bond via aryl to vinyl palladium 1,4-migration, *J. Am. Chem. Soc.*, 2016, **138**, 2897−2900. (*b*) Q. Wang, R. Chen, J. Lou, D. H. Zhang, Y.-G. Zhou and Z. Yu, Highly regioselective C–H alkylation of alkenes through an aryl to vinyl 1,4-palladium migration/C–C cleavage cascade, *ACS Catal.*, 2019, **9**, 11669−11675.

10. ^{1}H NMR and ^{13}C NMR spectra

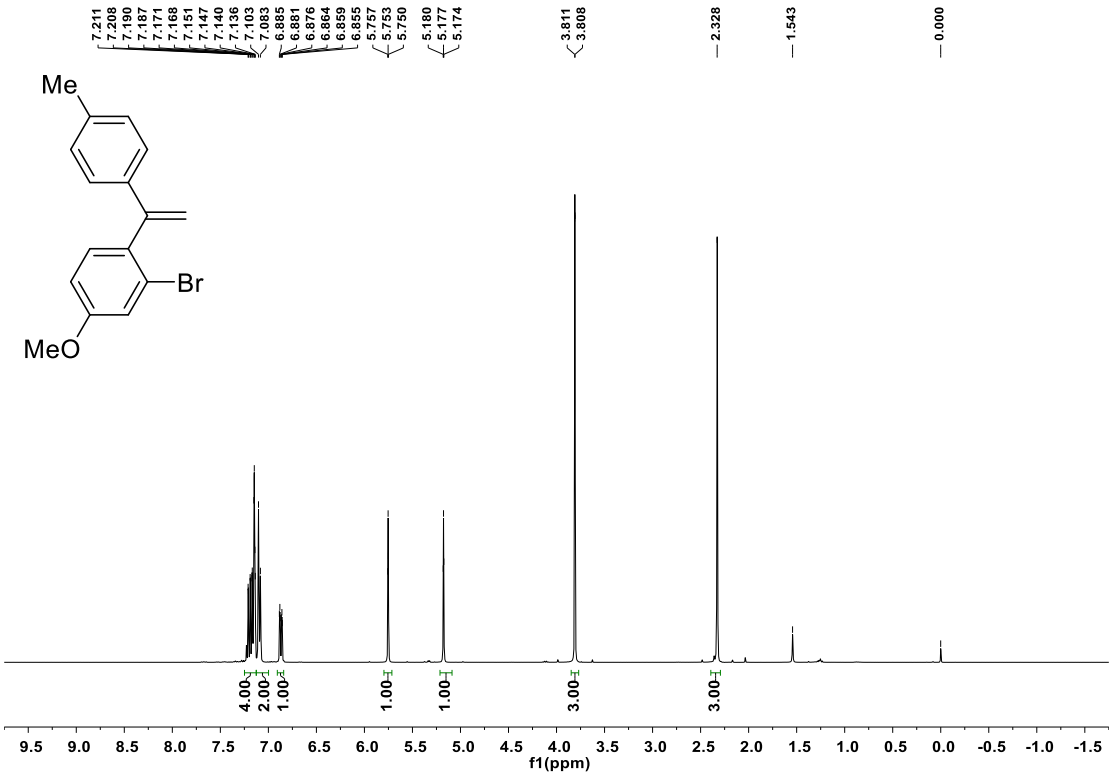
^{1}H NMR of **1f** in $CDCl_3$ (400 MHz)



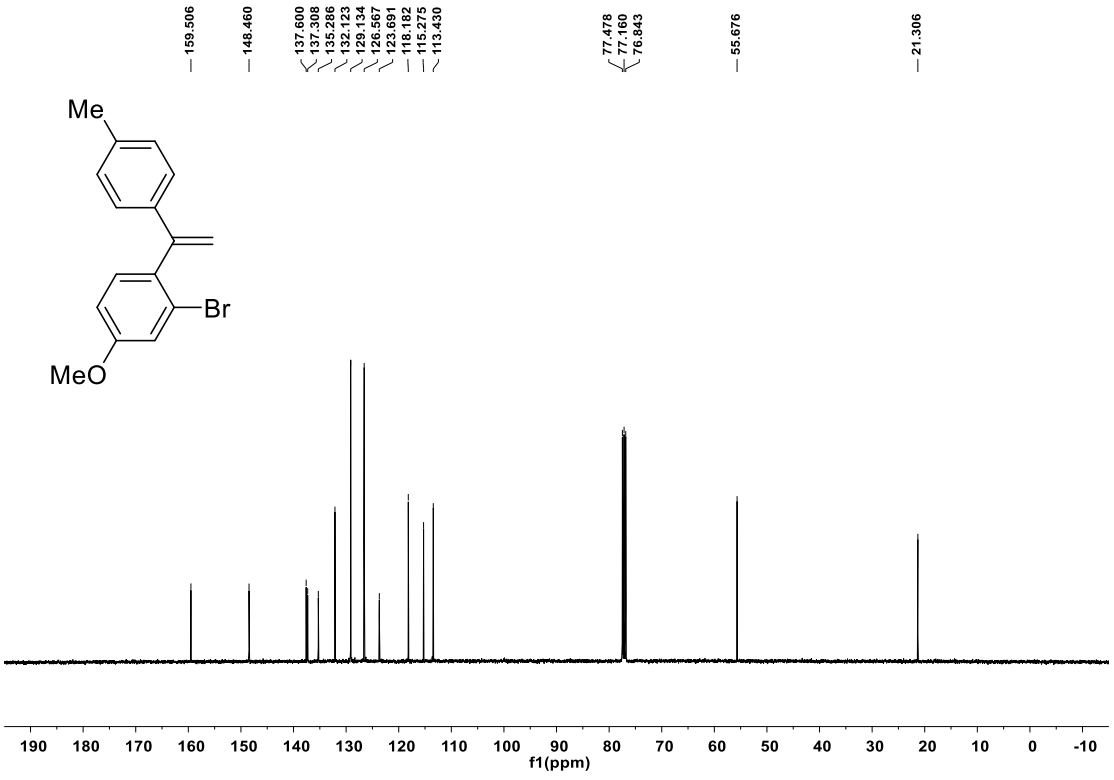
^{13}C NMR of **1f** in $CDCl_3$ (100 MHz)



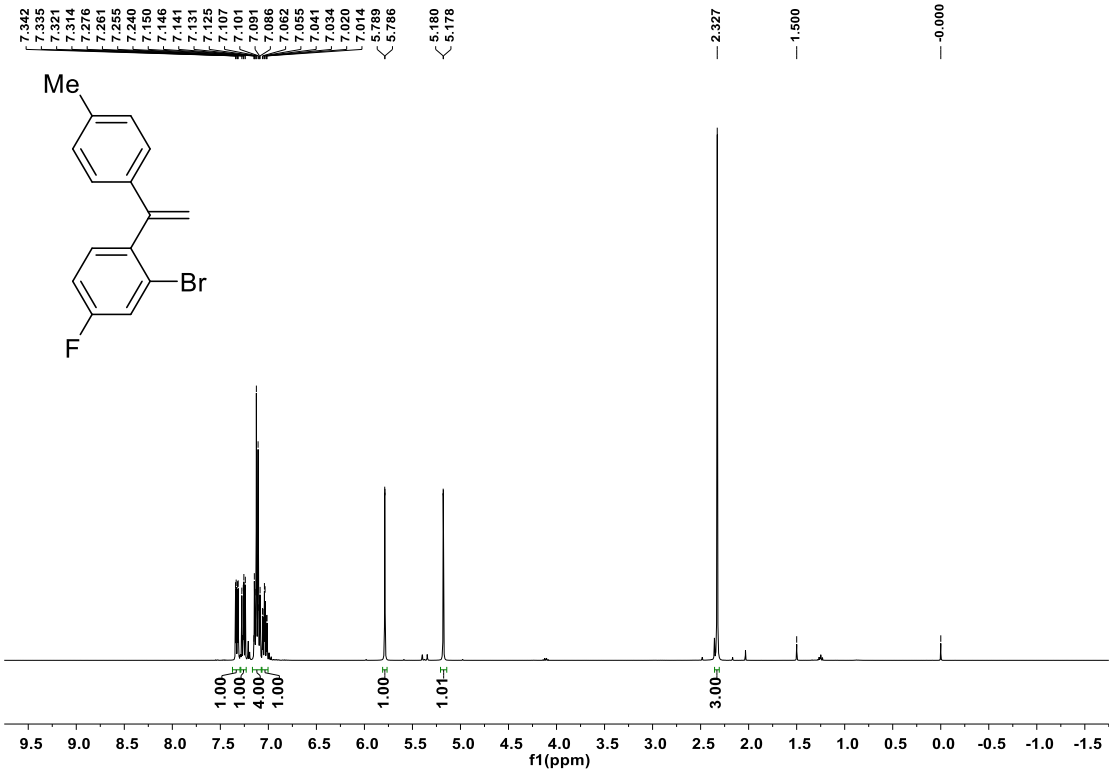
^{1}H NMR of **1u** in $CDCl_3$ (400 MHz)



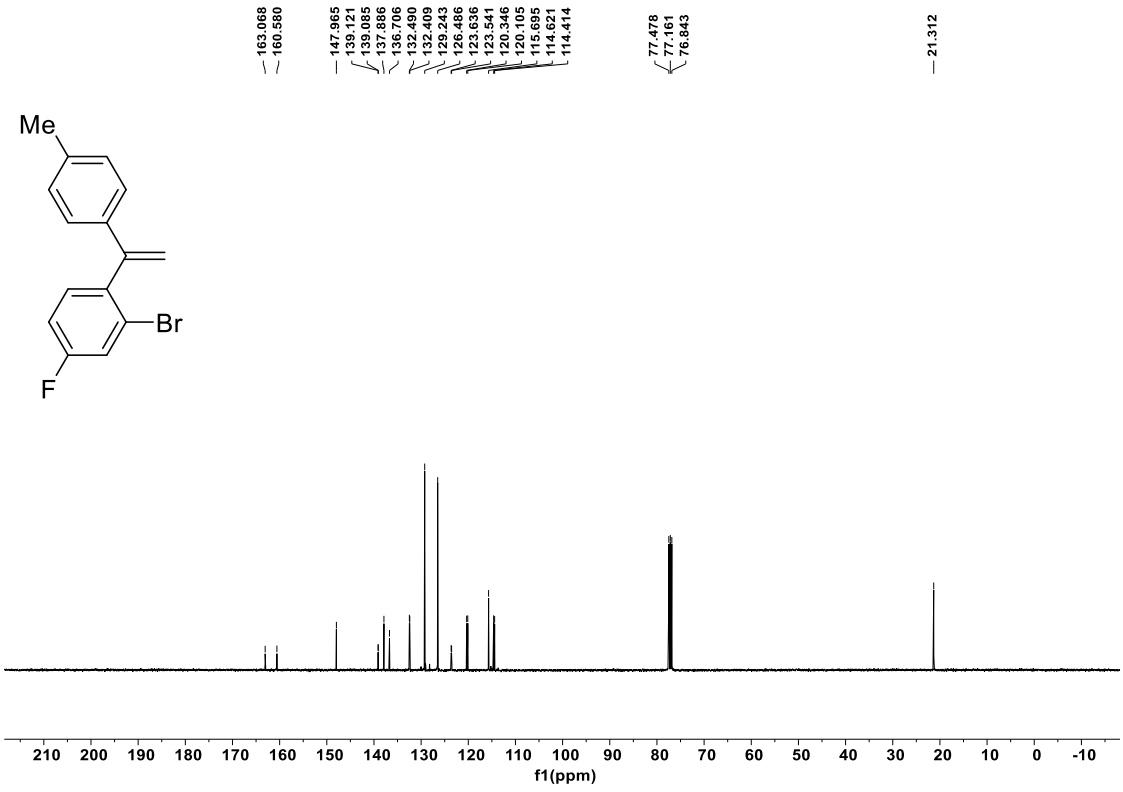
^{13}C NMR of **1u** in $CDCl_3$ (100 MHz)



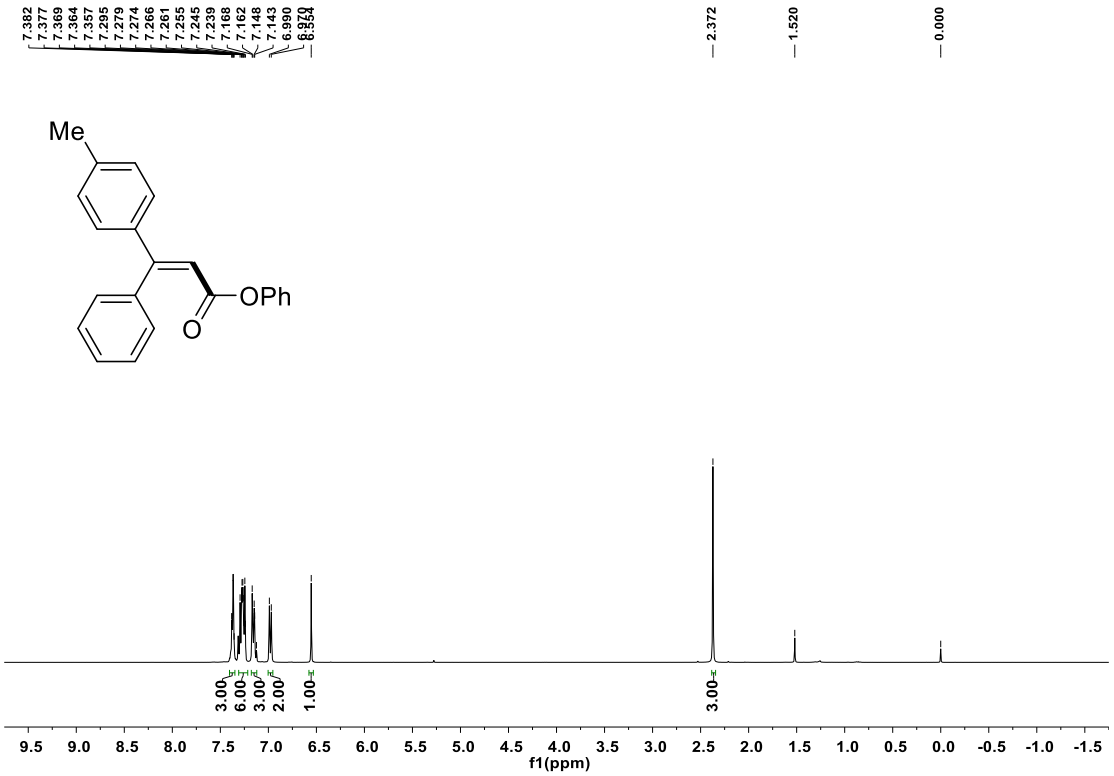
^{1}H NMR of **1v** in $CDCl_3$ (400 MHz)



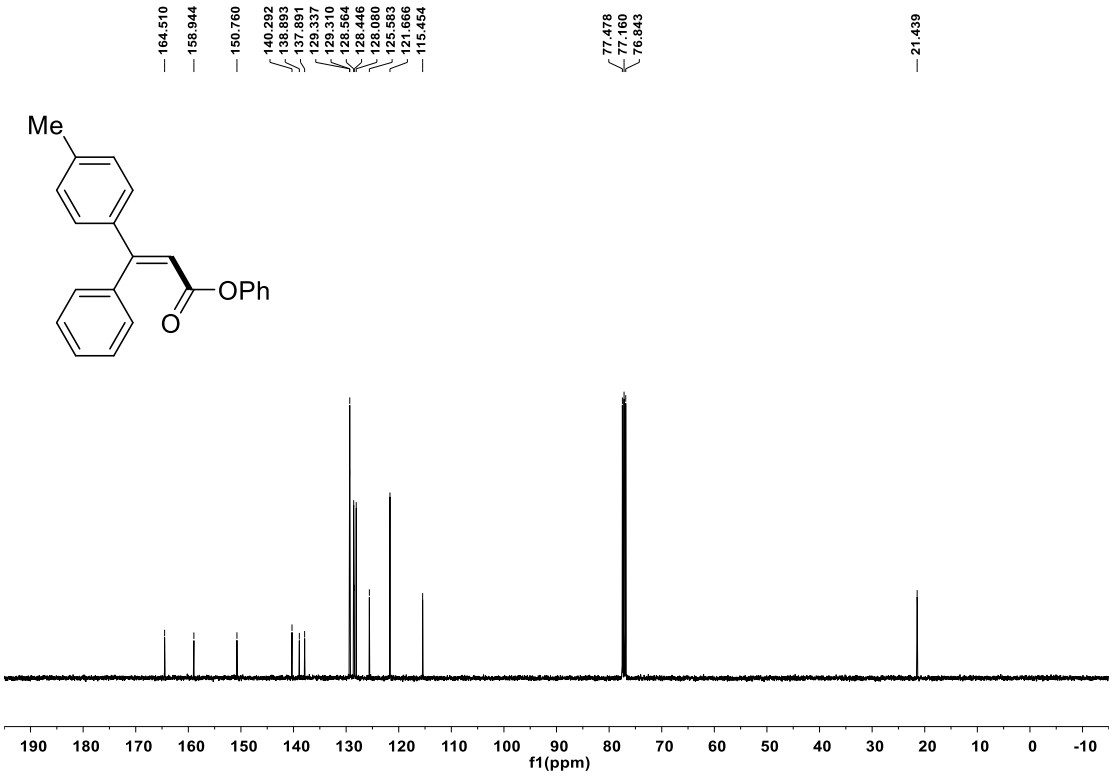
^{13}C NMR of **1v** in $CDCl_3$ (100 MHz)



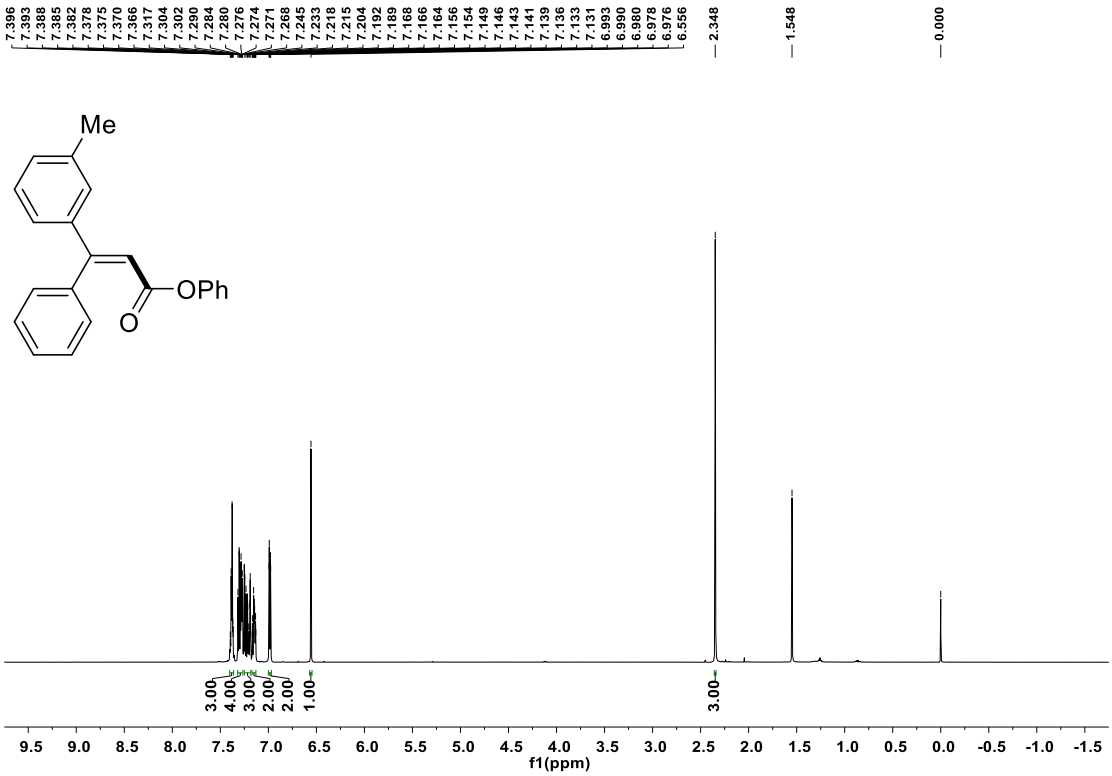
^{1}H NMR of **3a** in $CDCl_3$ (400 MHz)



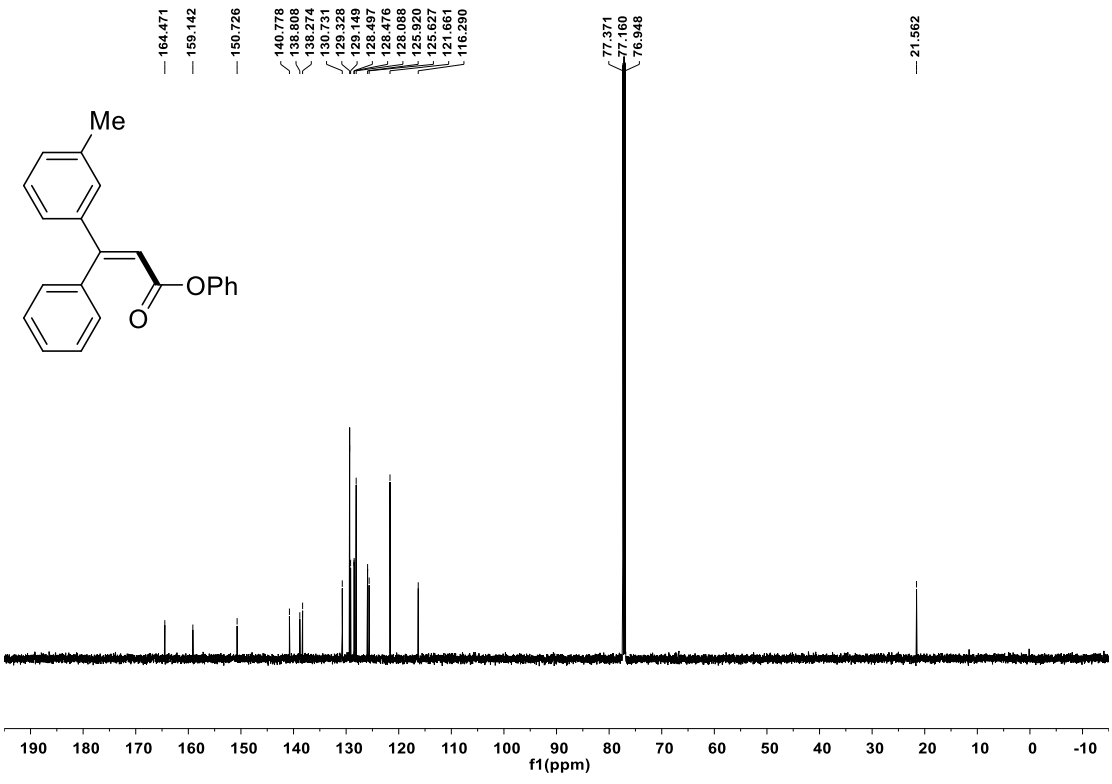
^{13}C NMR of **3a** in $CDCl_3$ (100 MHz)



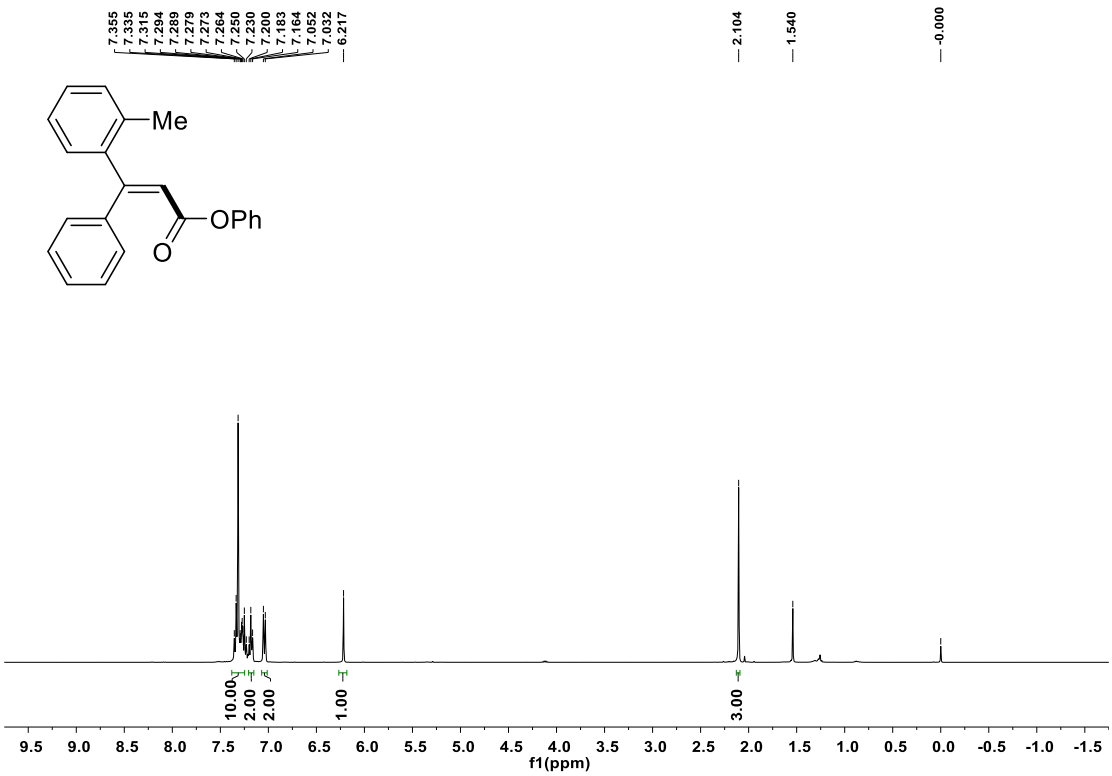
^{1}H NMR of **3b** in $CDCl_3$ (600 MHz)



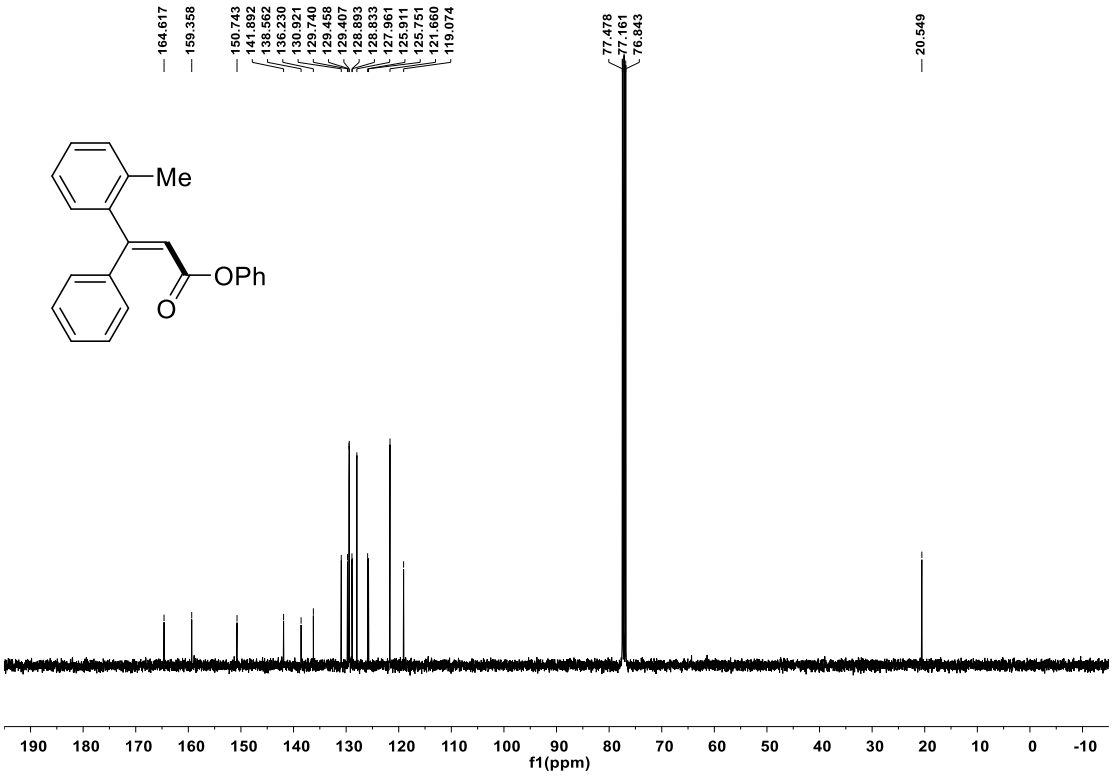
^{13}C NMR of **3b** in $CDCl_3$ (150 MHz)



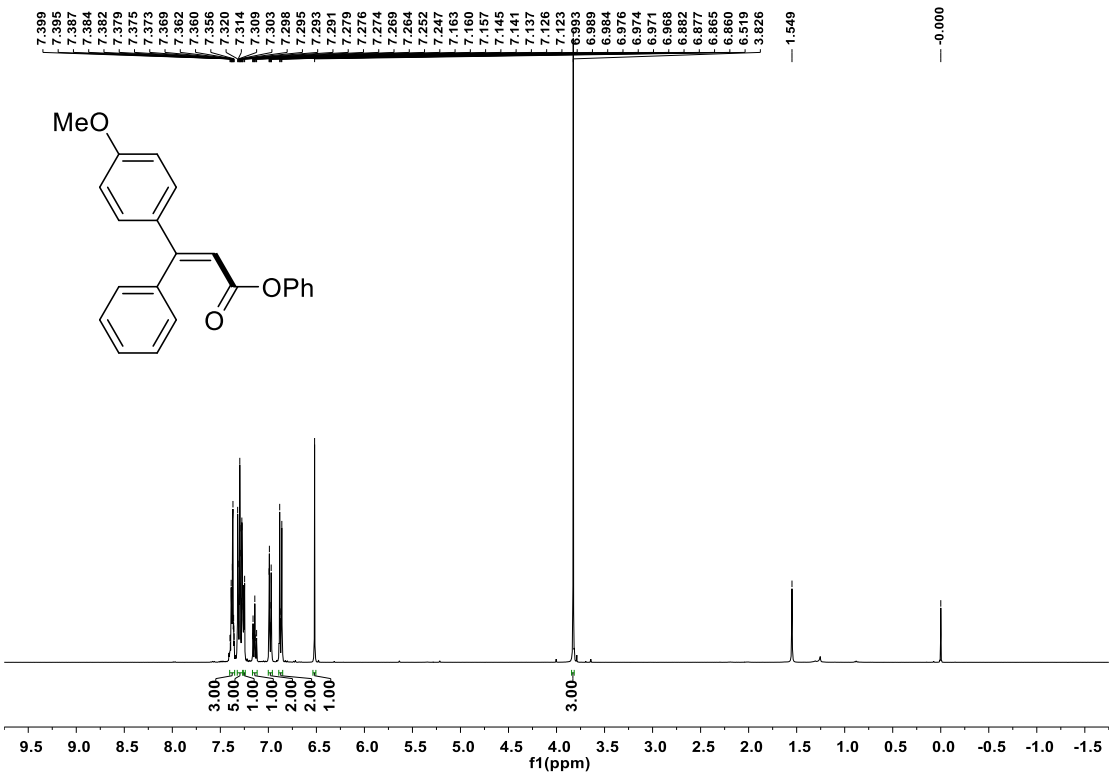
^{1}H NMR of **3c** in $CDCl_3$ (400 MHz)



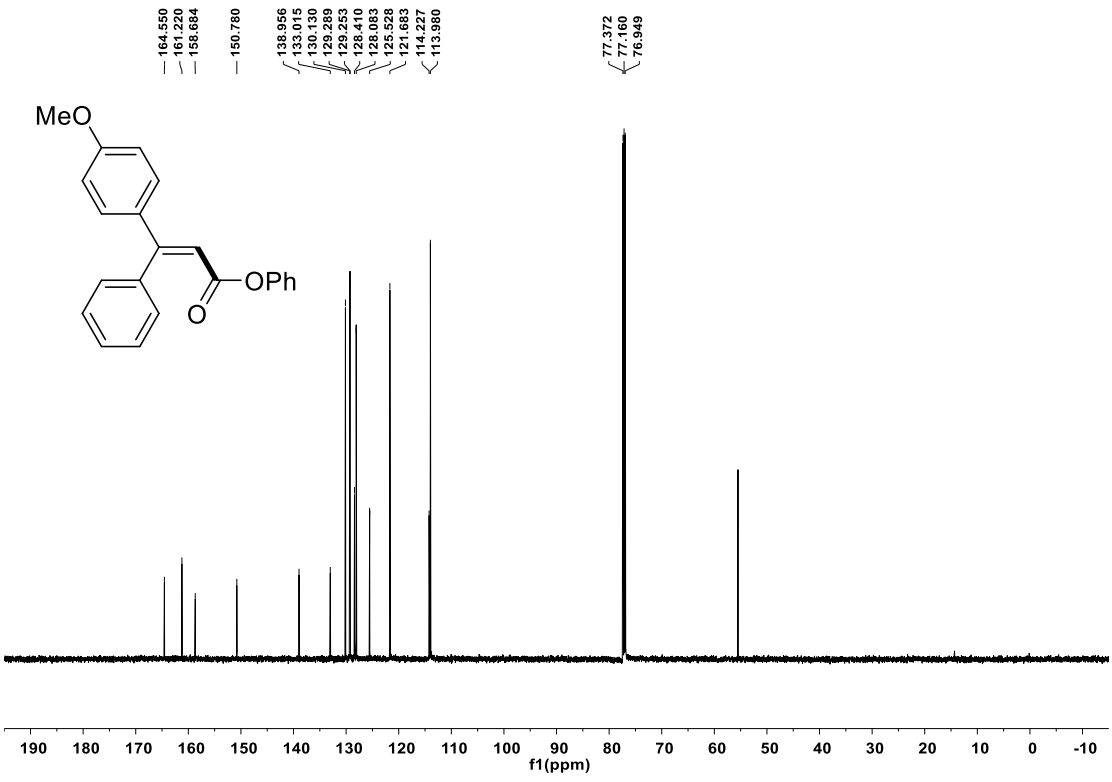
^{13}C NMR of **3c** in $CDCl_3$ (100 MHz)



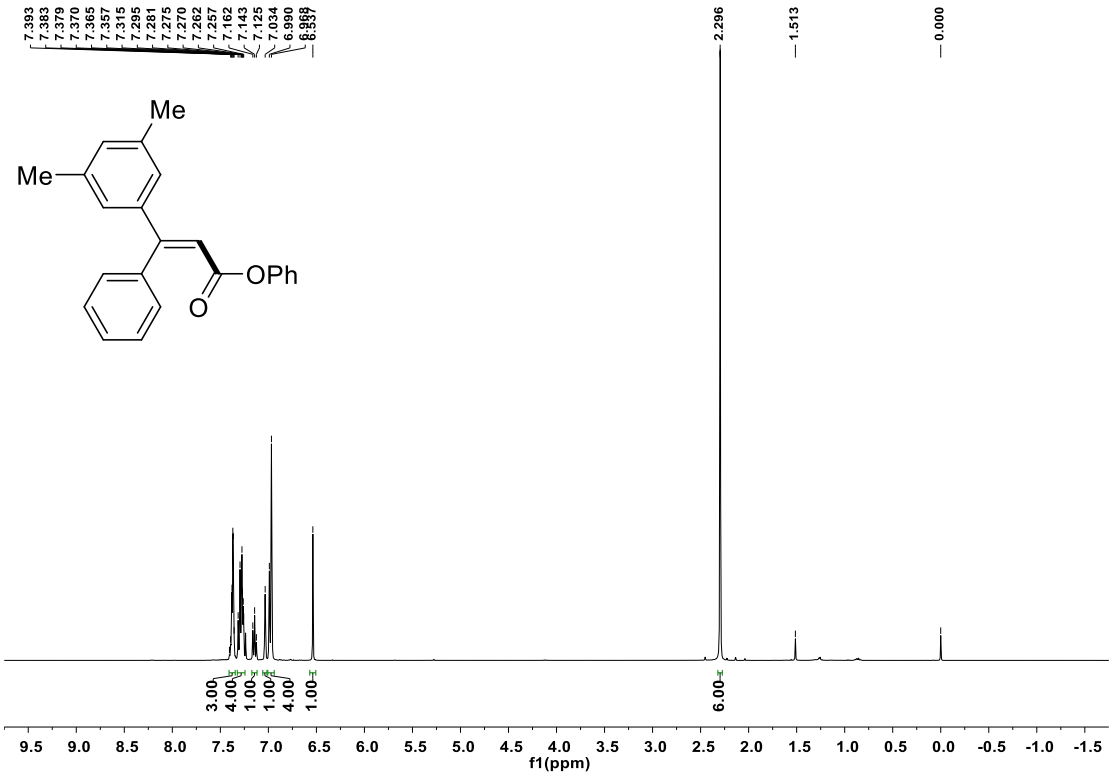
^{1}H NMR of **3d** in $CDCl_3$ (400 MHz)



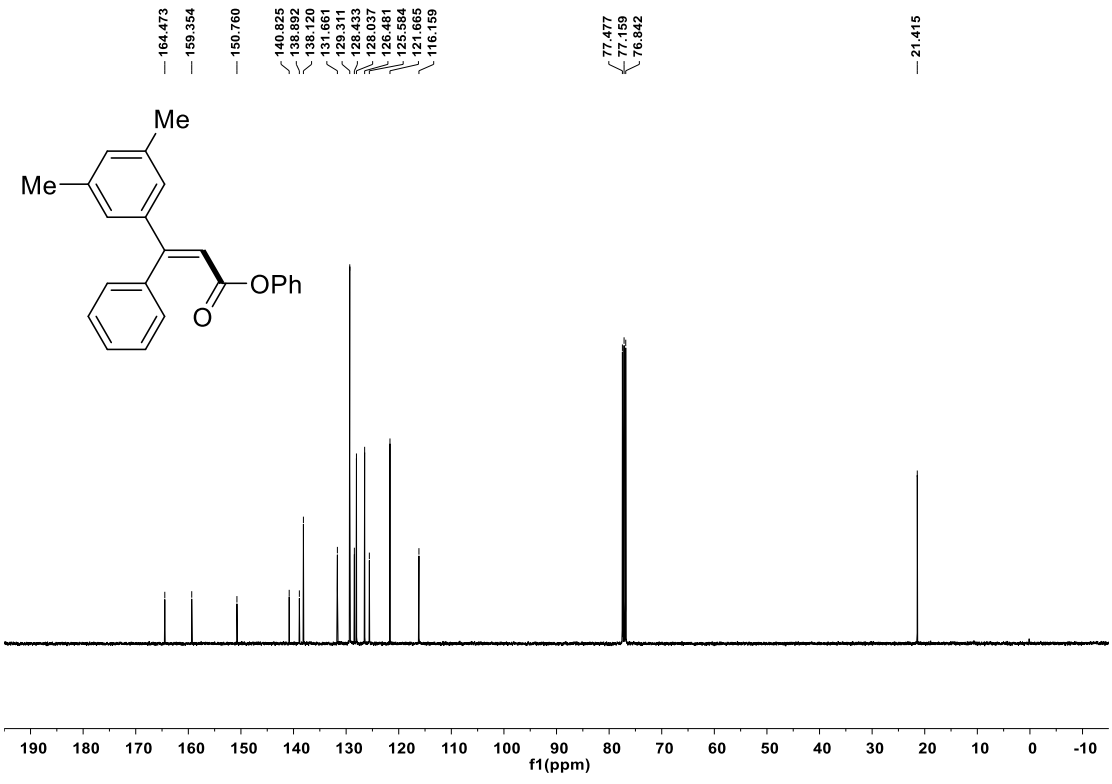
^{13}C NMR of **3d** in $CDCl_3$ (150 MHz)



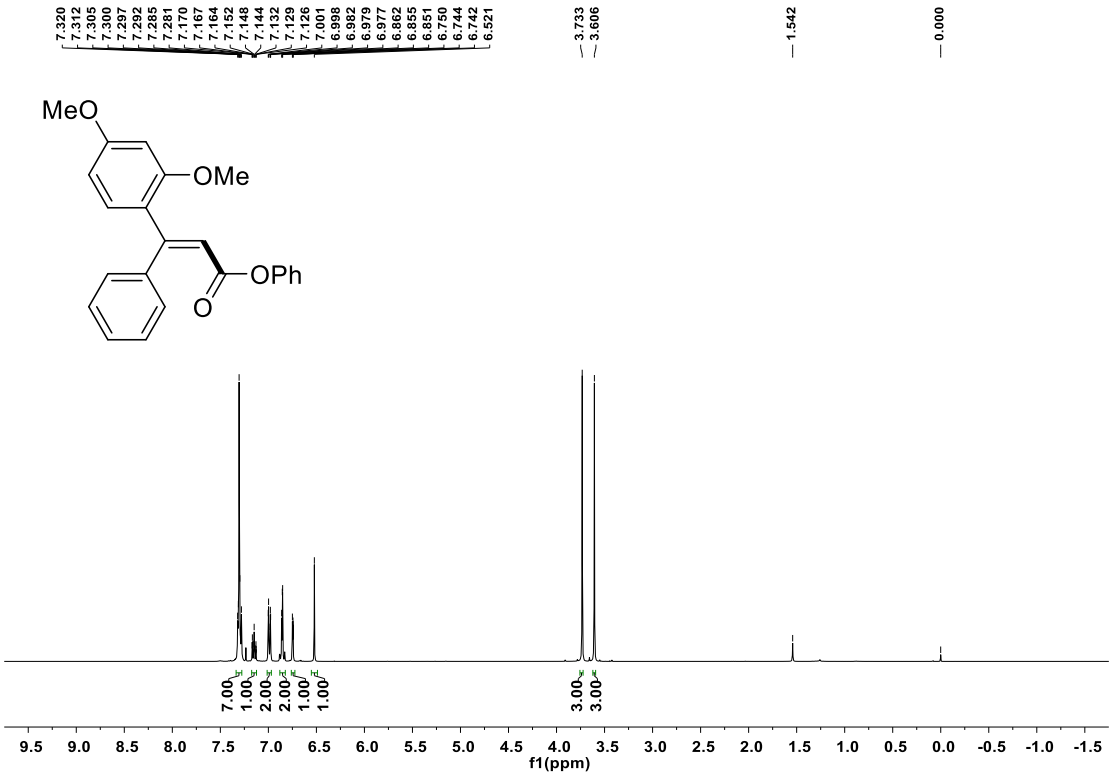
^{1}H NMR of **3e** in $CDCl_3$ (400 MHz)



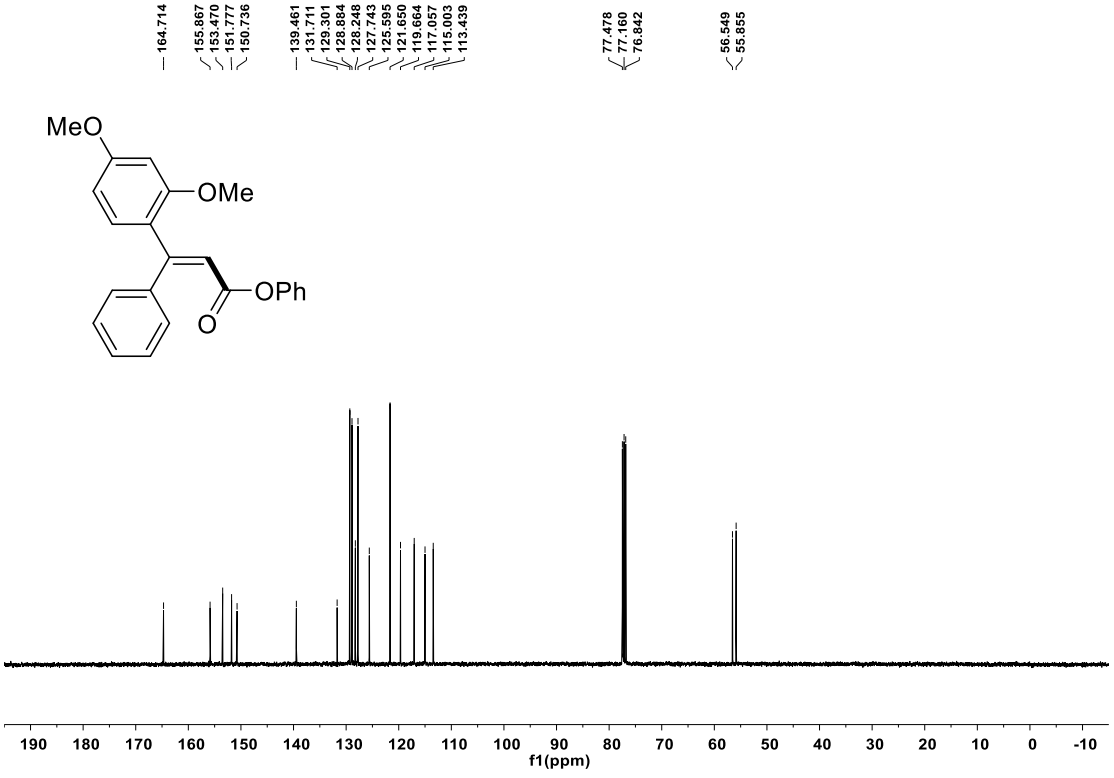
^{13}C NMR of **3e** in $CDCl_3$ (100 MHz)



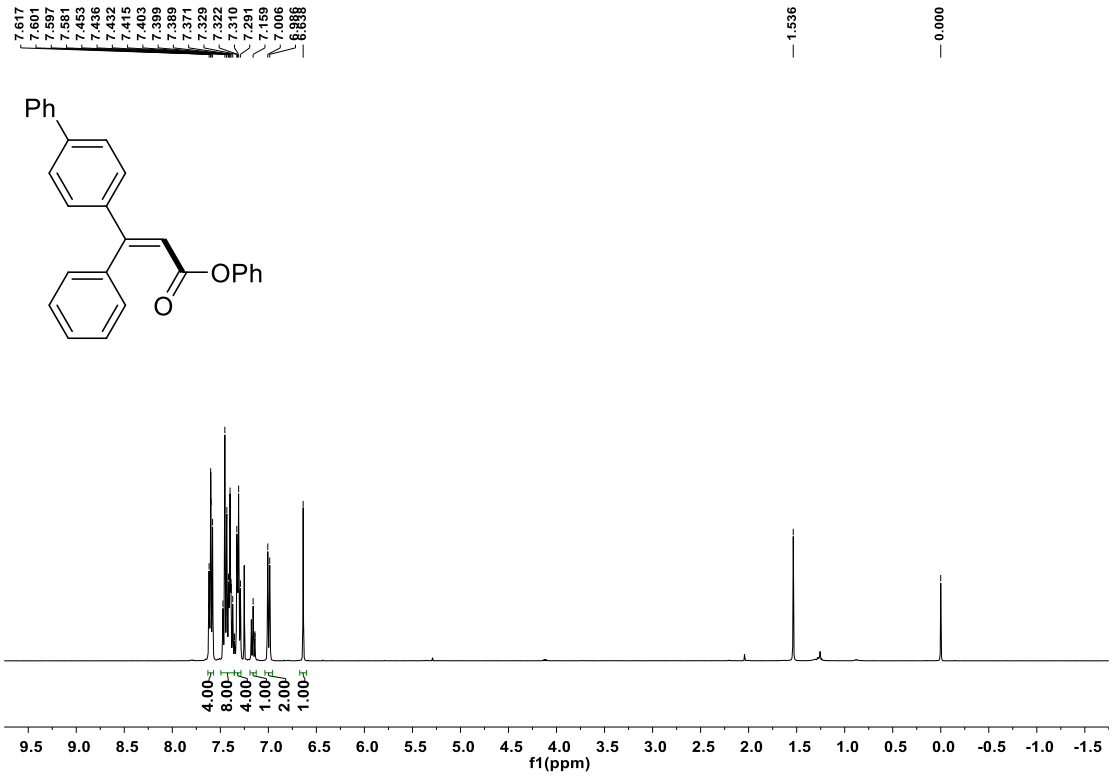
^{1}H NMR of **3f** in $CDCl_3$ (400 MHz)



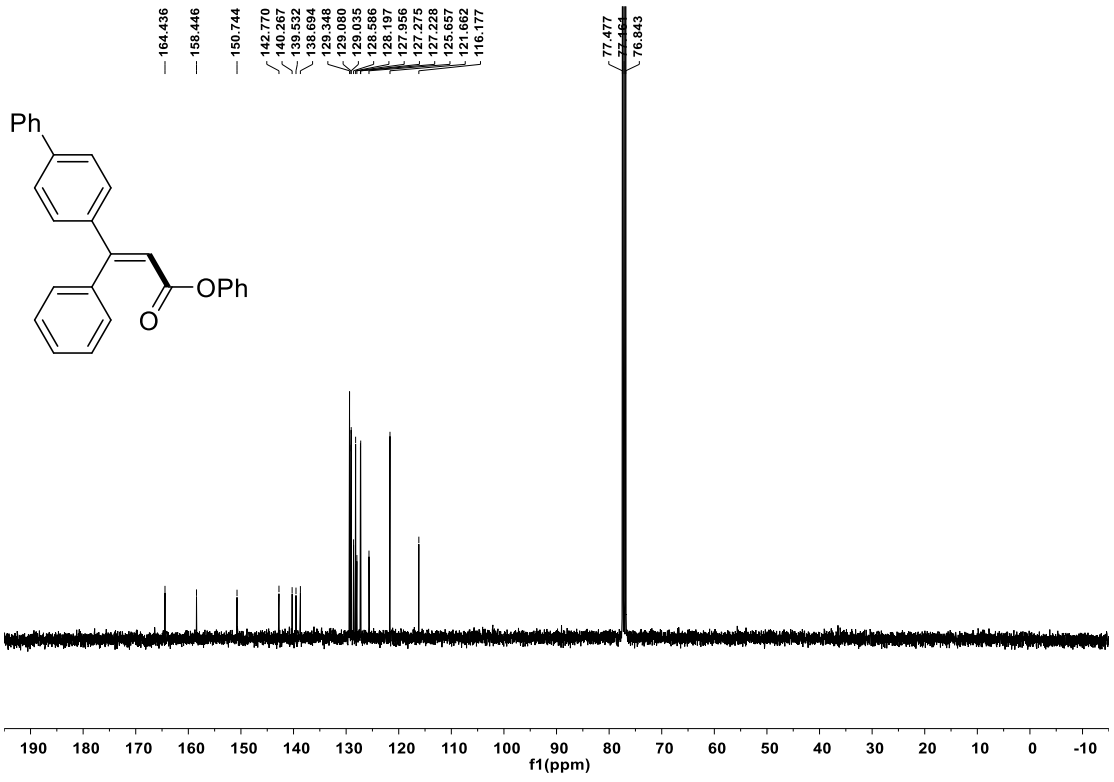
^{13}C NMR of **3f** in $CDCl_3$ (100 MHz)



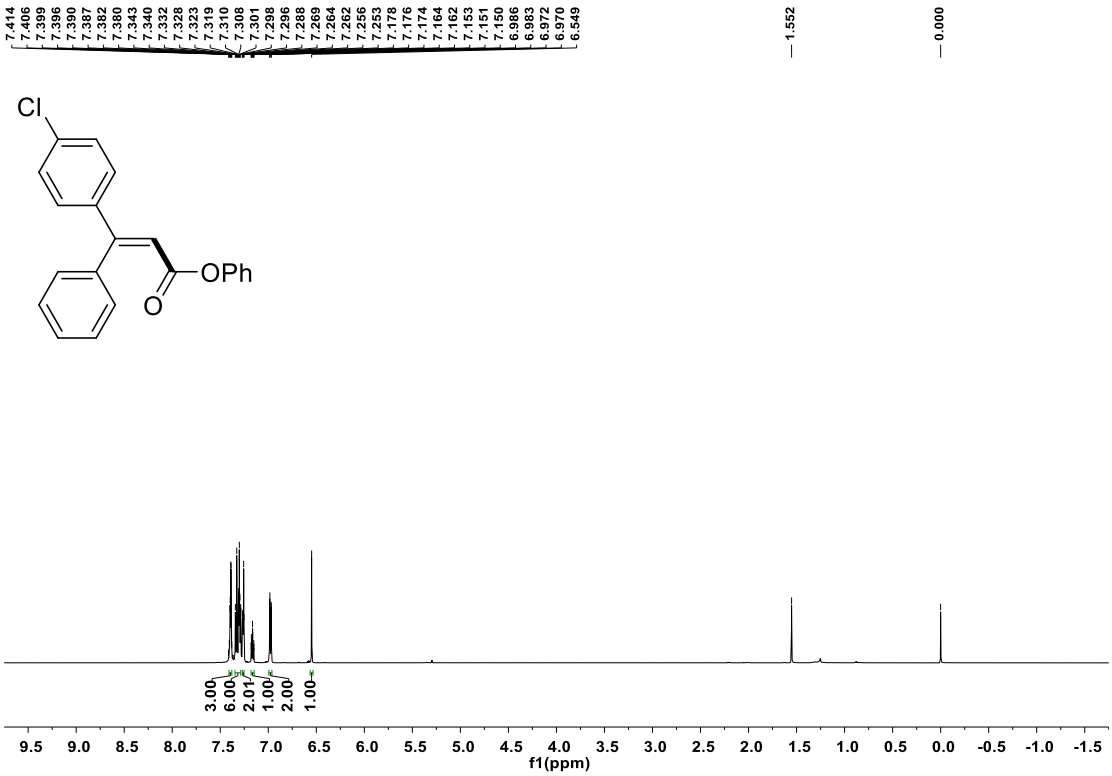
^{1}H NMR of **3g** in $CDCl_3$ (400 MHz)



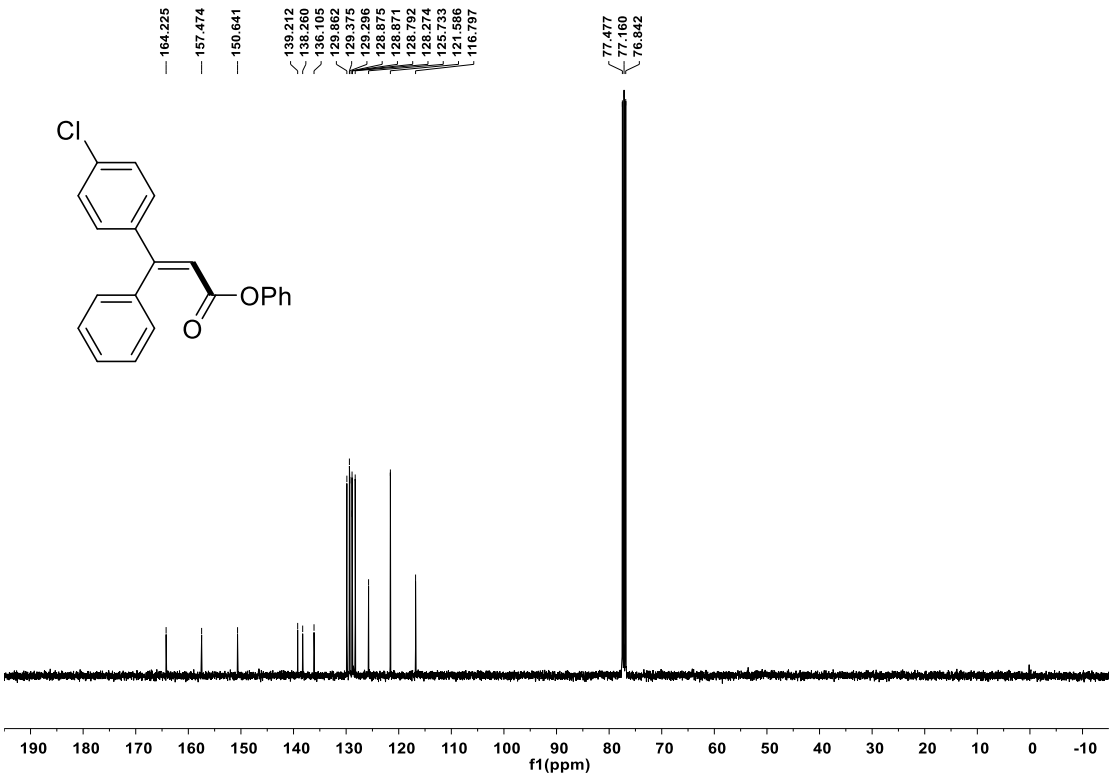
^{13}C NMR of **3g** in $CDCl_3$ (100 MHz)



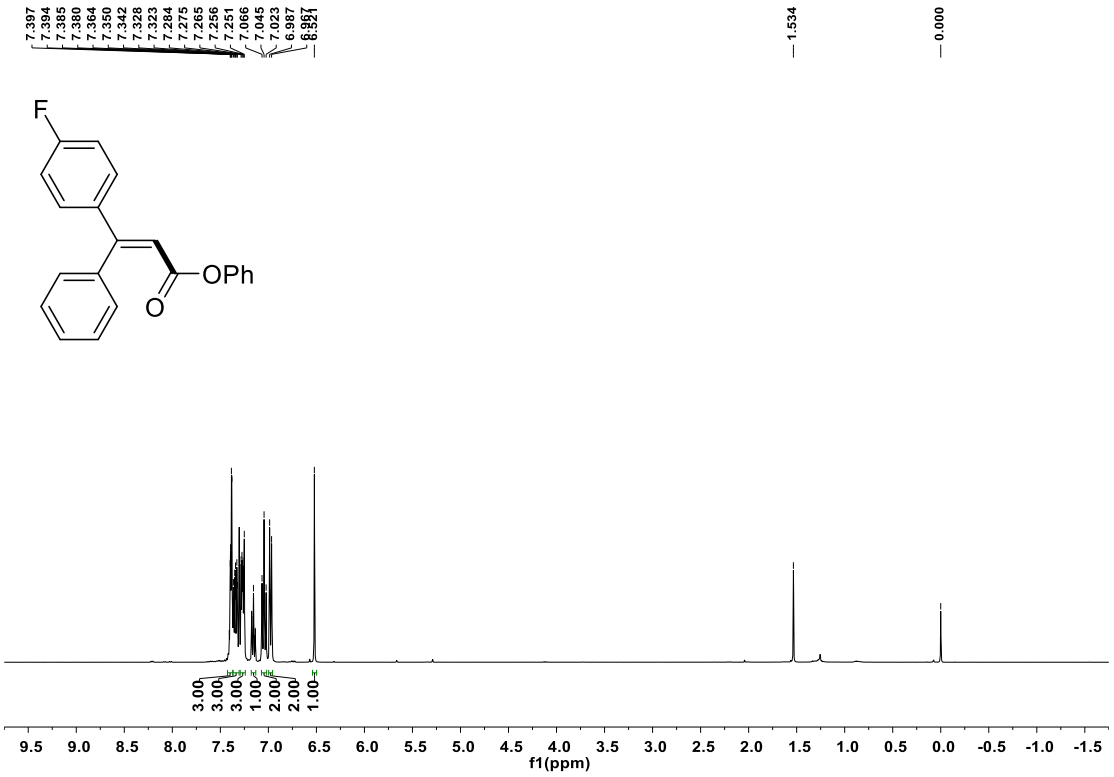
^{1}H NMR of **3h** in $CDCl_3$ (600 MHz)



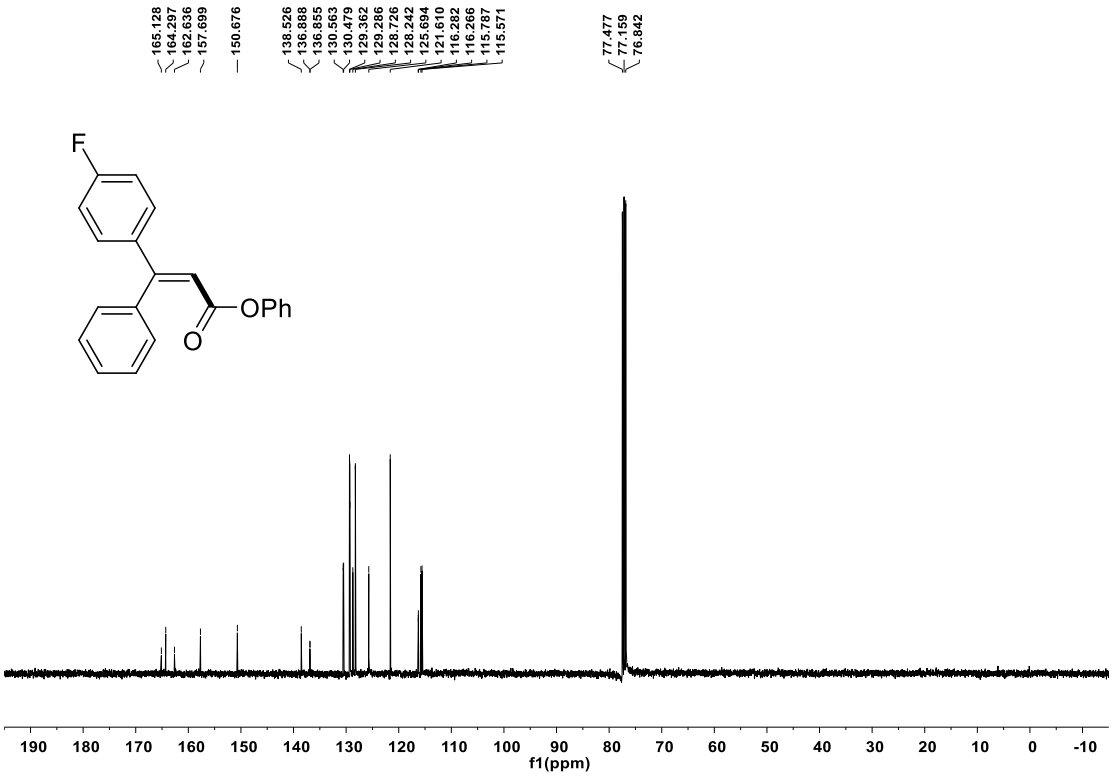
^{13}C NMR of **3h** in $CDCl_3$ (100 MHz)



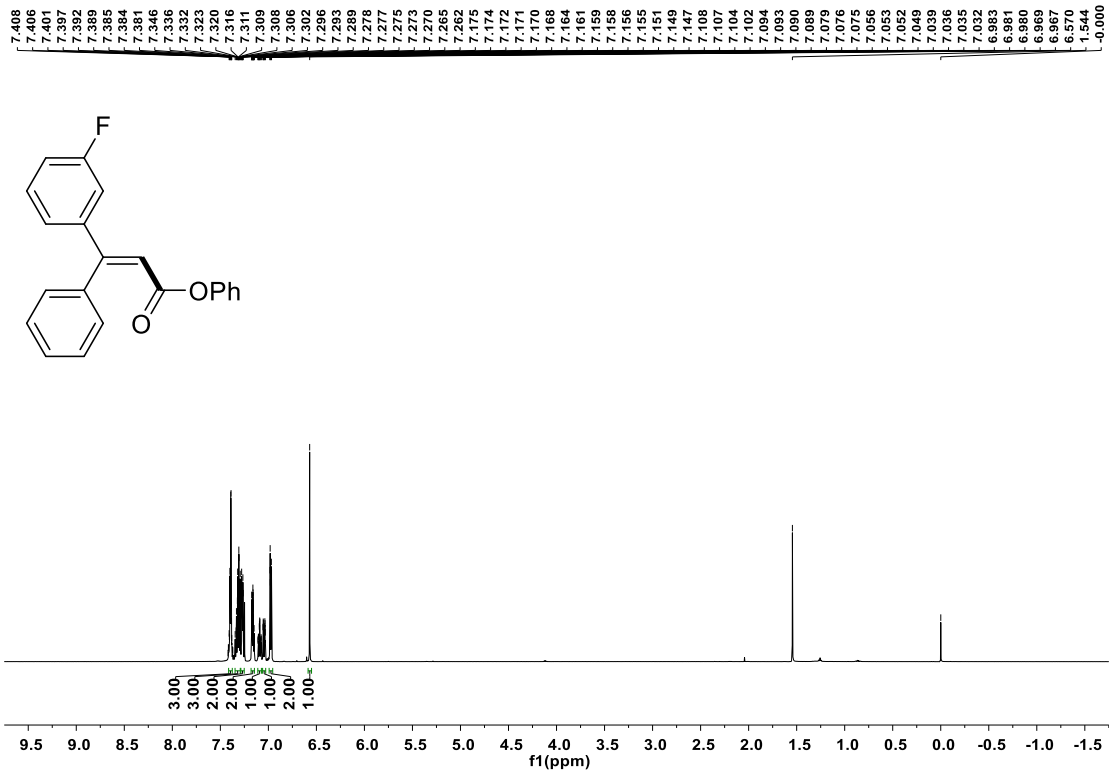
^{1}H NMR of **3i** in $CDCl_3$ (400 MHz)



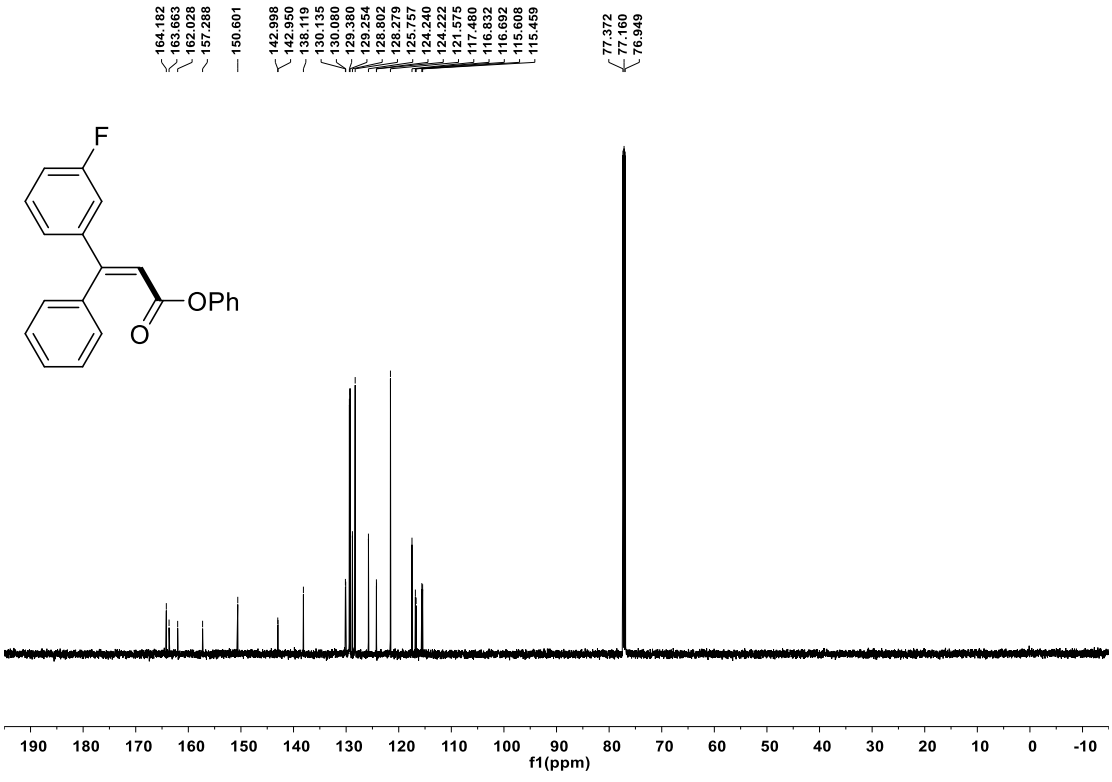
^{13}C NMR of **3i** in $CDCl_3$ (100 MHz)



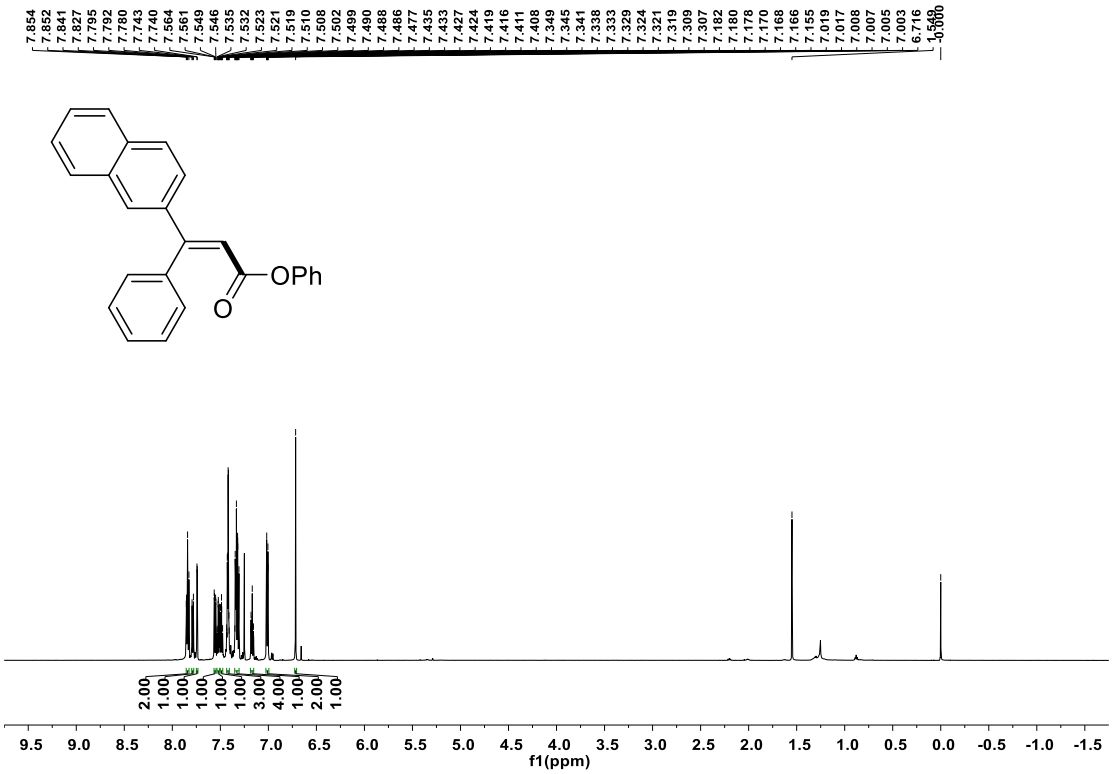
^{1}H NMR of **3j** in $CDCl_3$ (600 MHz)



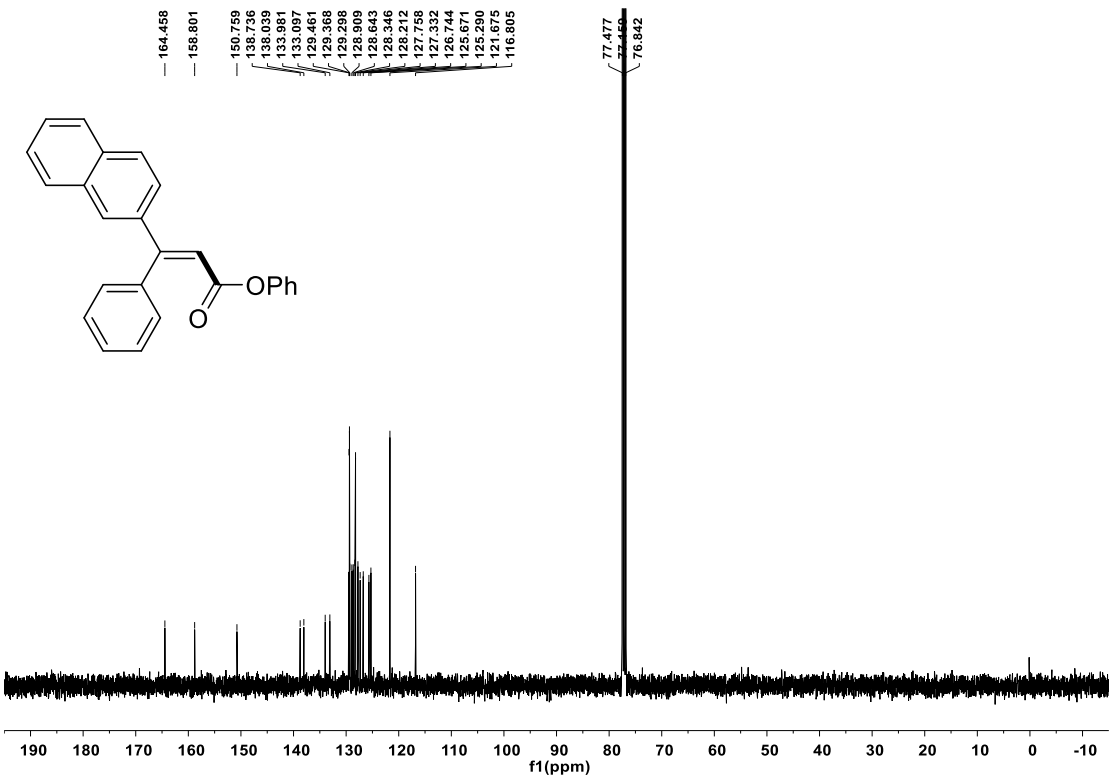
^{13}C NMR of **3j** in $CDCl_3$ (150 MHz)



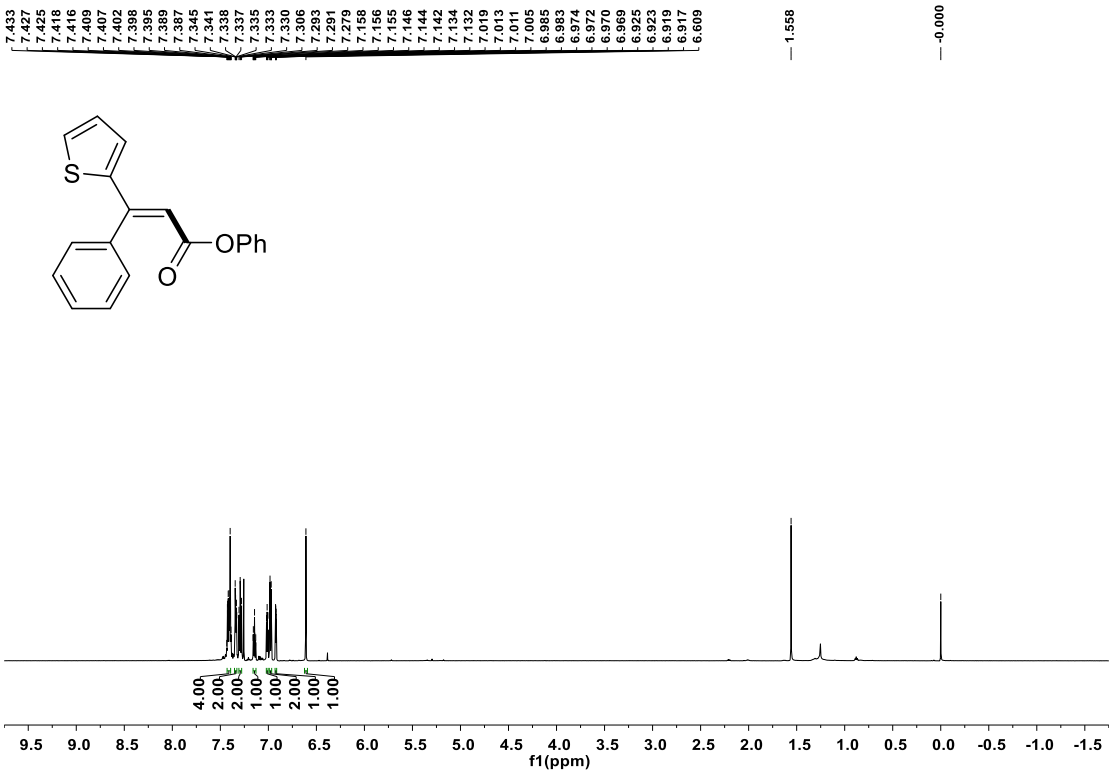
^{1}H NMR of **3k** in $CDCl_3$ (600 MHz)



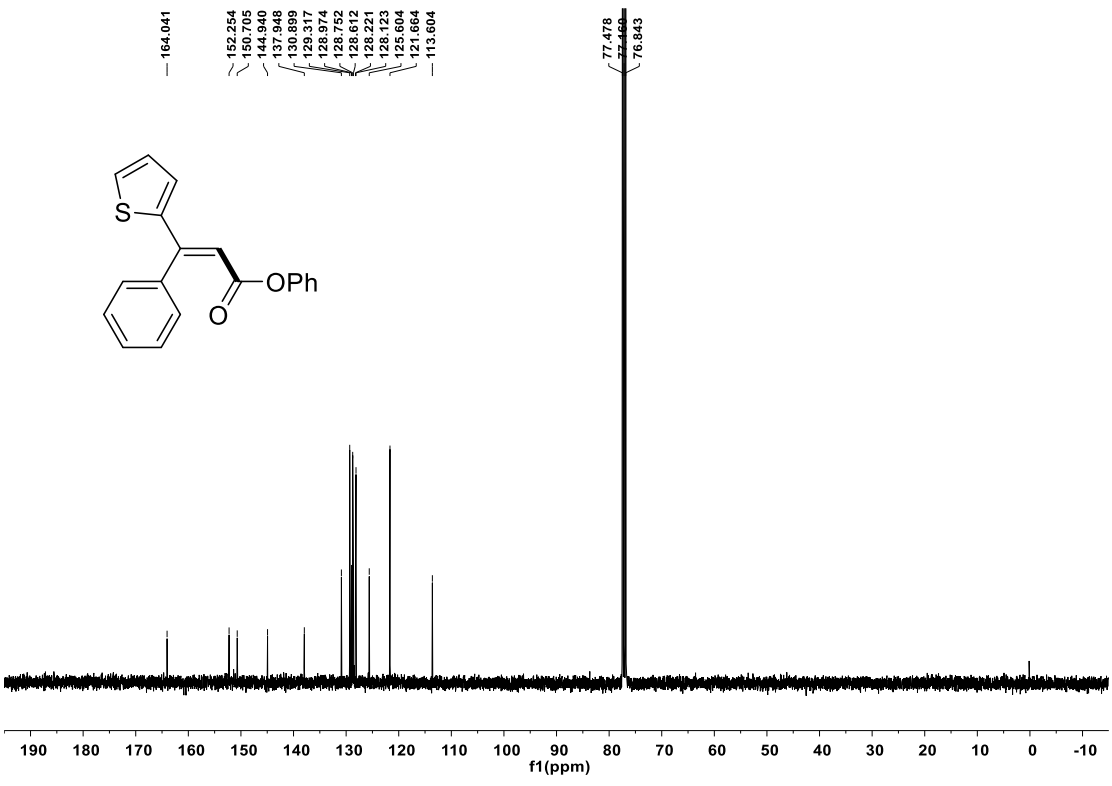
^{13}C NMR of **3k** in $CDCl_3$ (100 MHz)



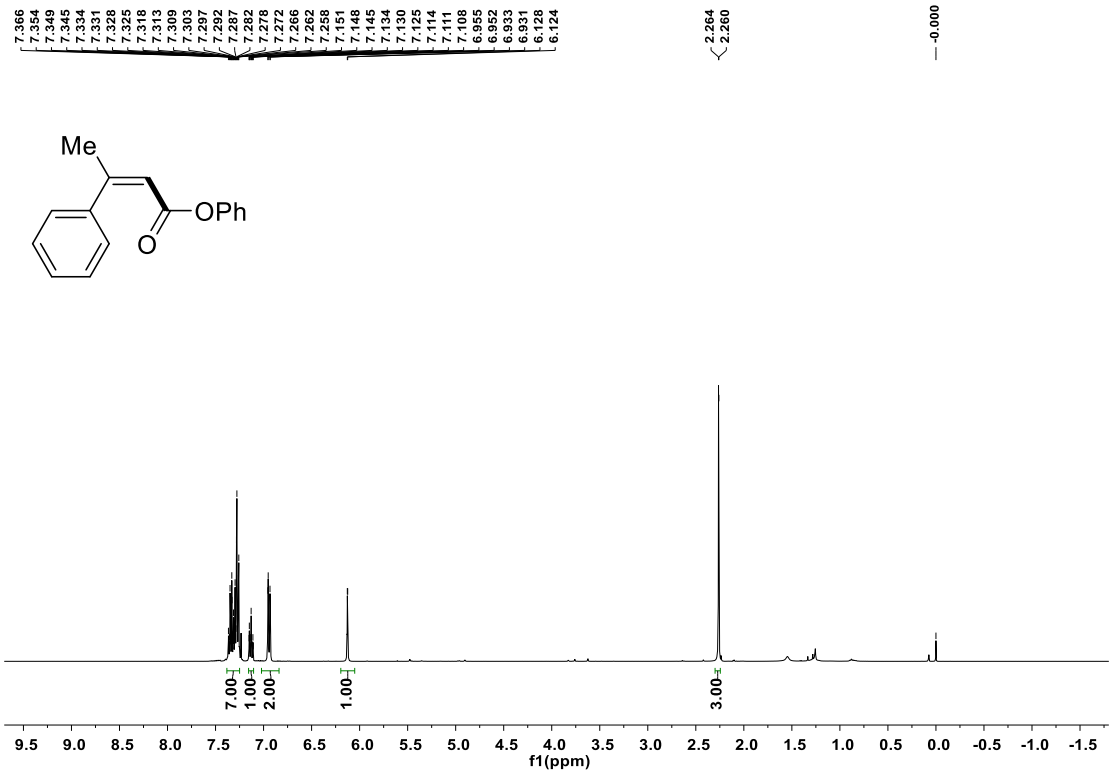
^{1}H NMR of **3l** in $CDCl_3$ (600 MHz)



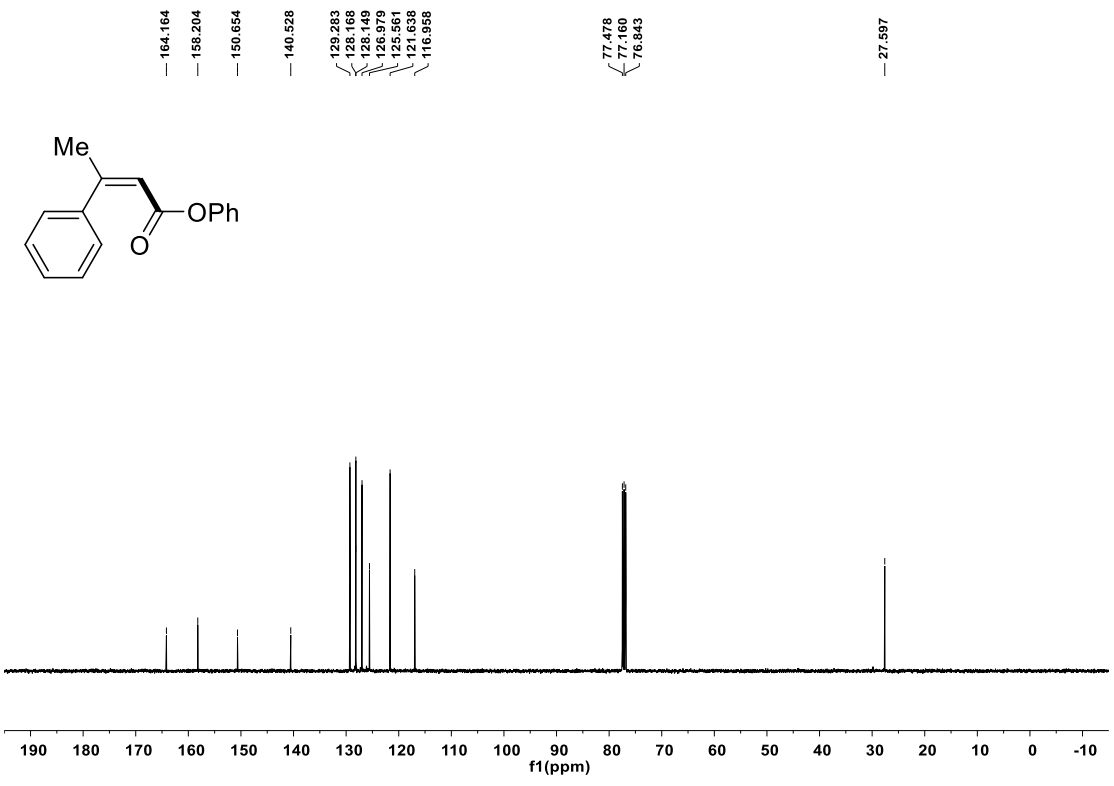
^{13}C NMR of **3l** in $CDCl_3$ (100 MHz)



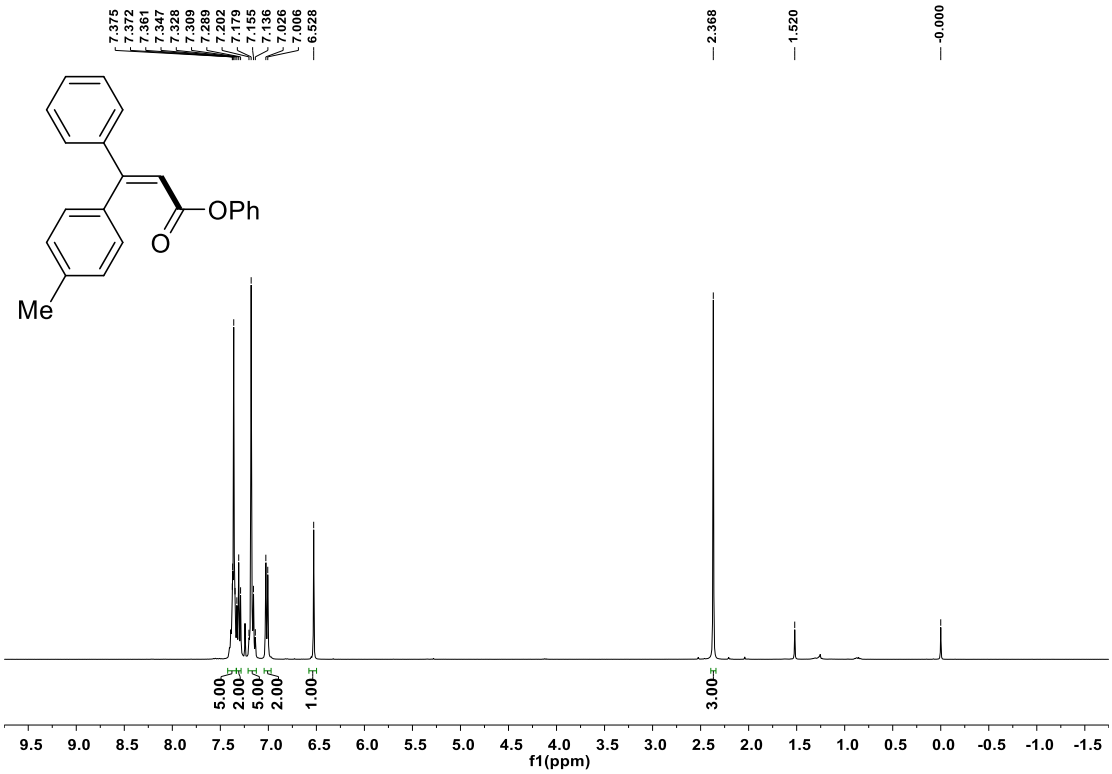
^{1}H NMR of **3m** in $CDCl_3$ (400 MHz)



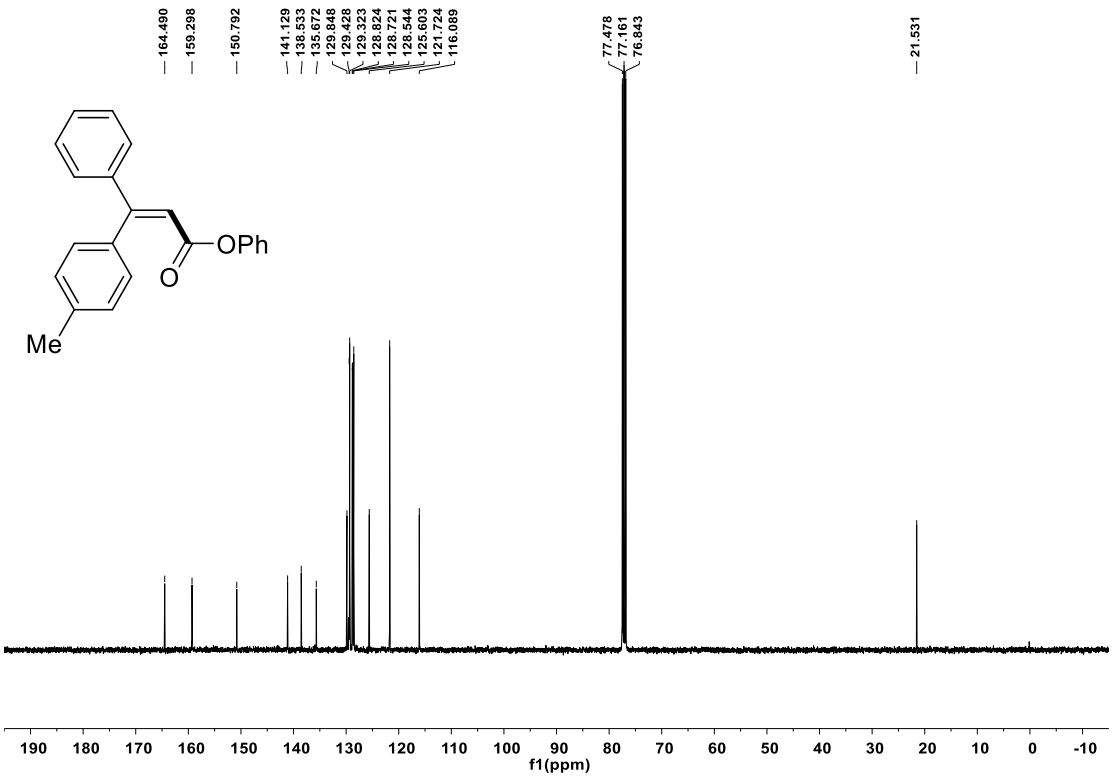
^{13}C NMR of **3m** in $CDCl_3$ (100 MHz)



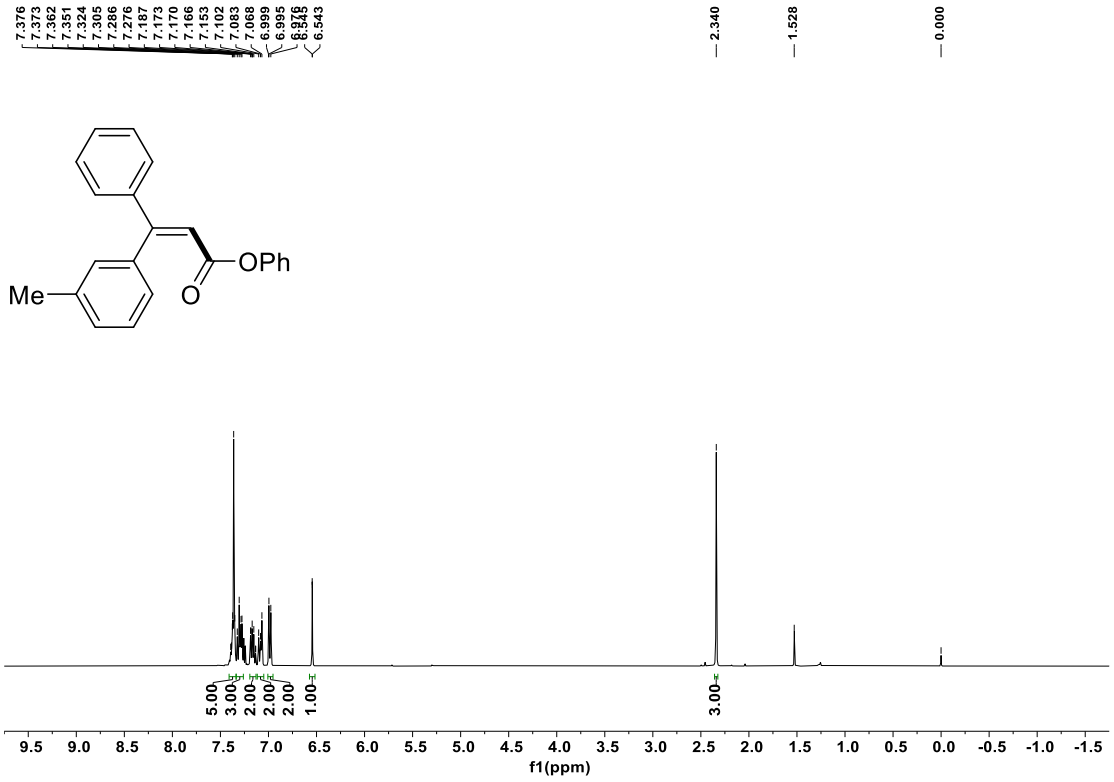
^{1}H NMR of **3n** in $CDCl_3$ (400 MHz)



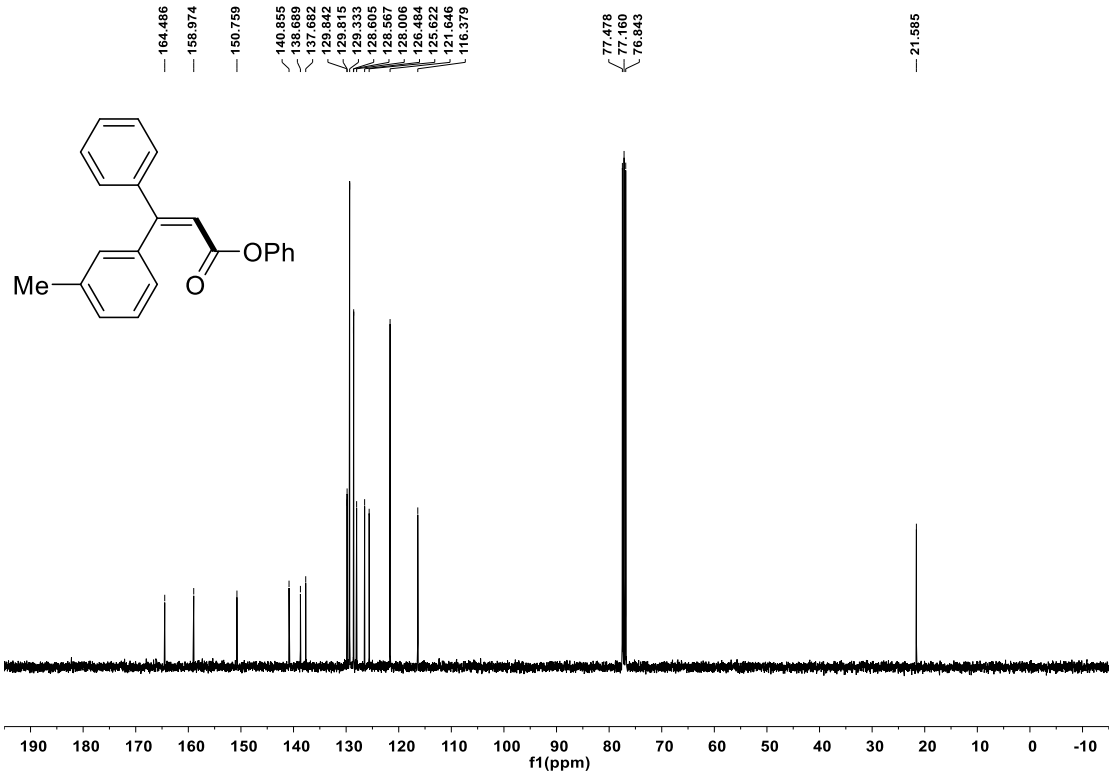
^{13}C NMR of **3n** in $CDCl_3$ (100 MHz)



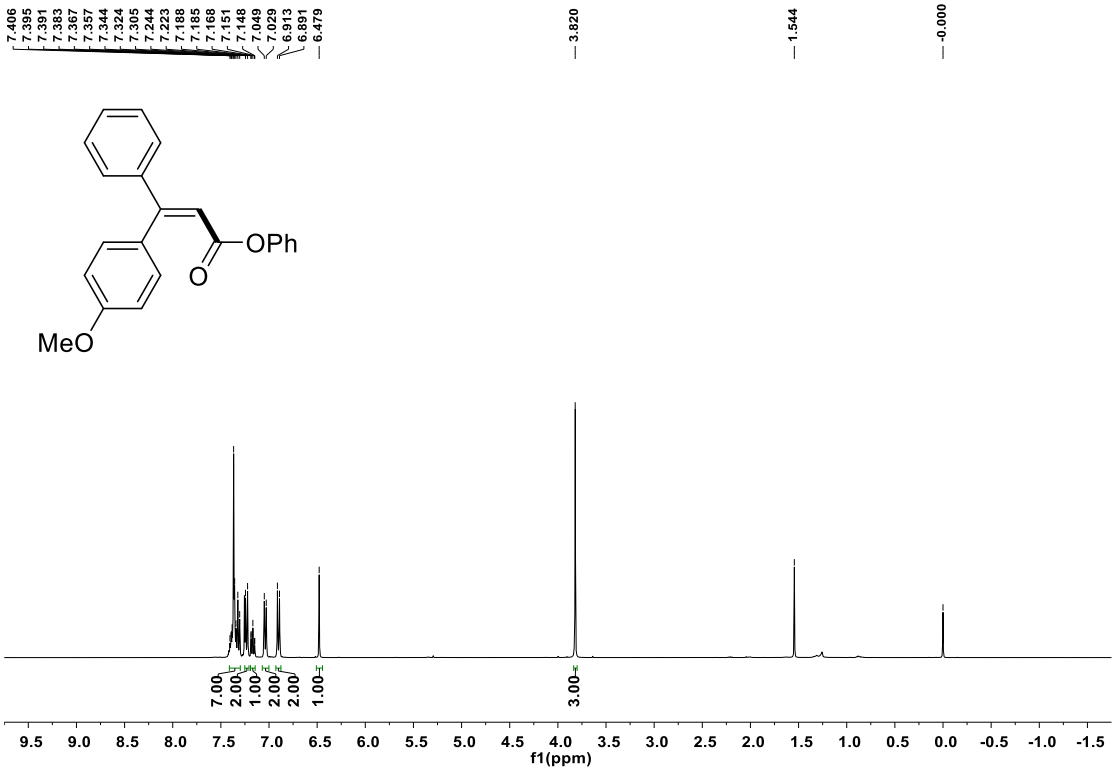
^{1}H NMR of **3o** in $CDCl_3$ (400 MHz)



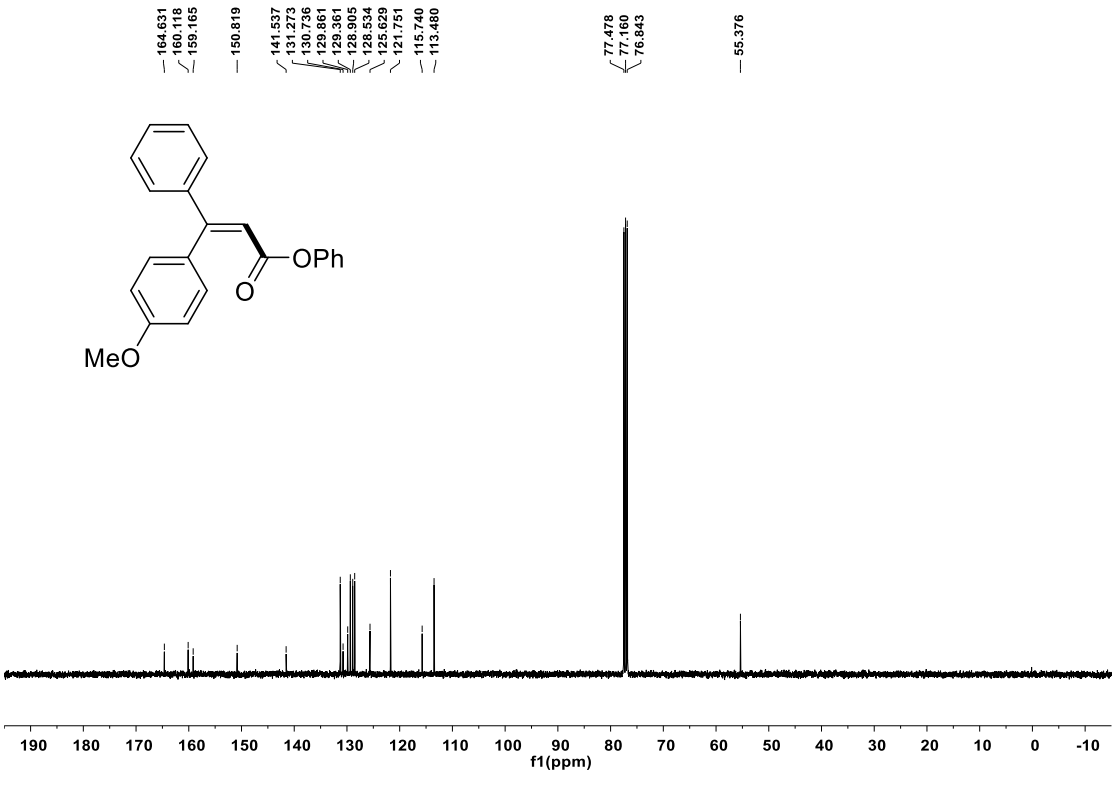
^{13}C NMR of **3o** in $CDCl_3$ (100 MHz)



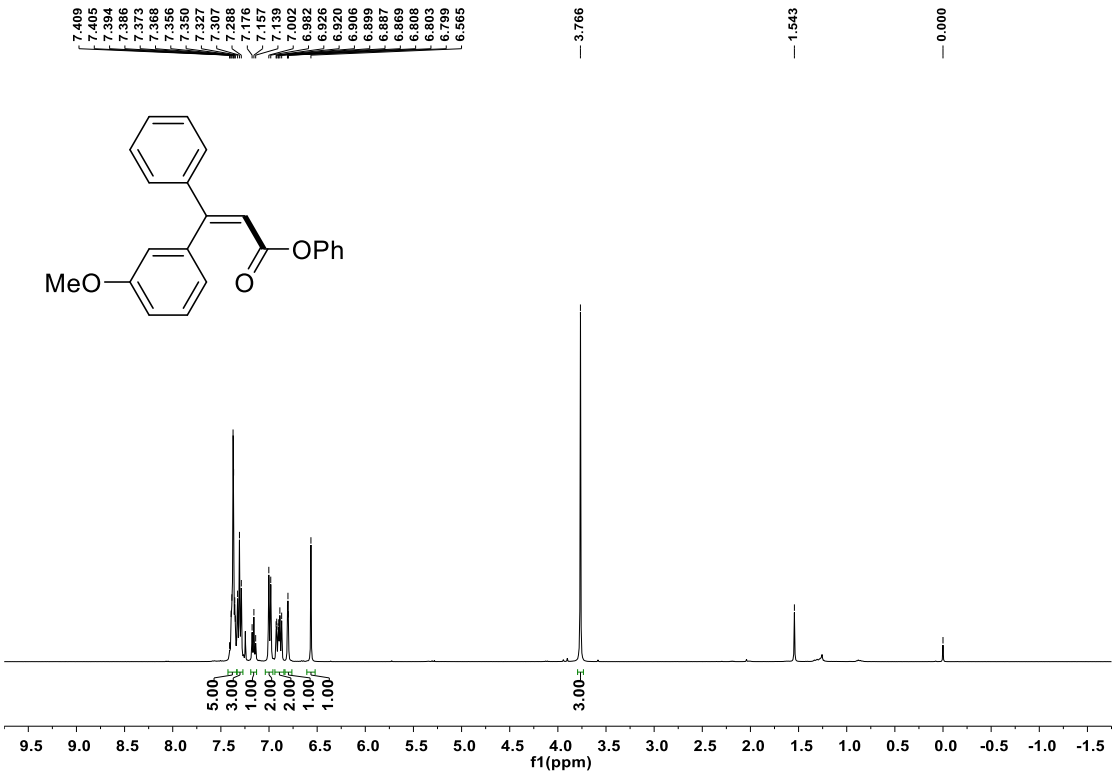
^{1}H NMR of **3p** in $CDCl_3$ (400 MHz)



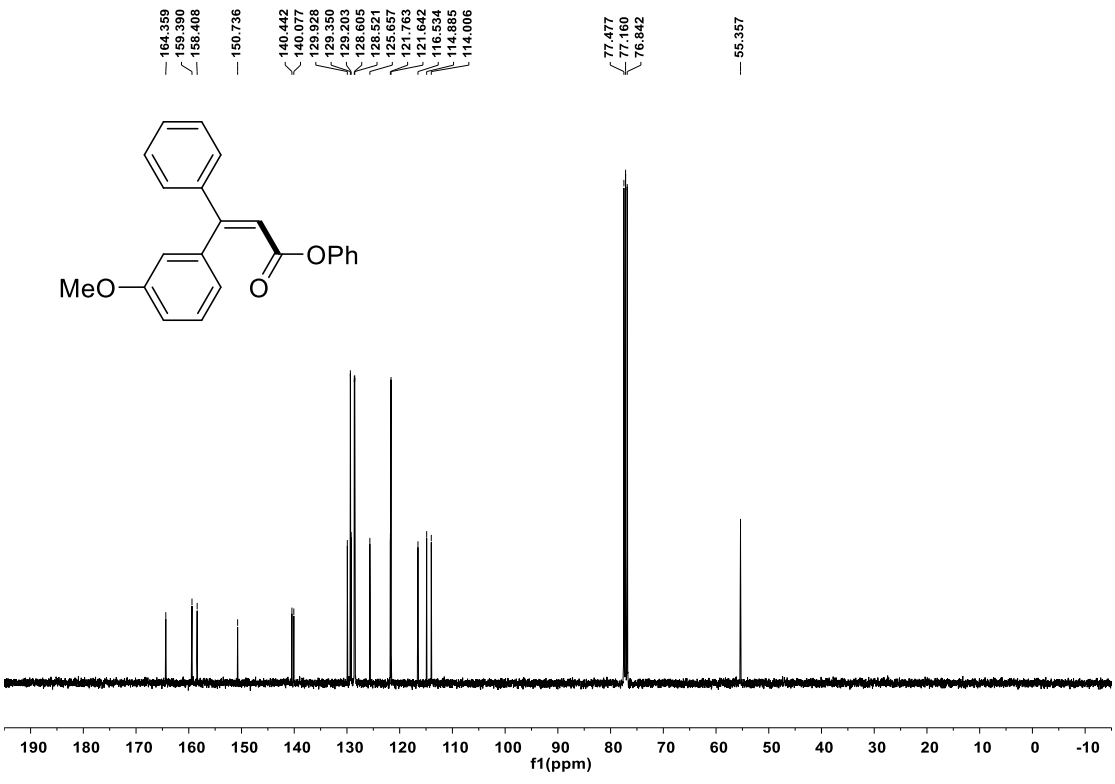
^{13}C NMR of **3p** in $CDCl_3$ (100 MHz)



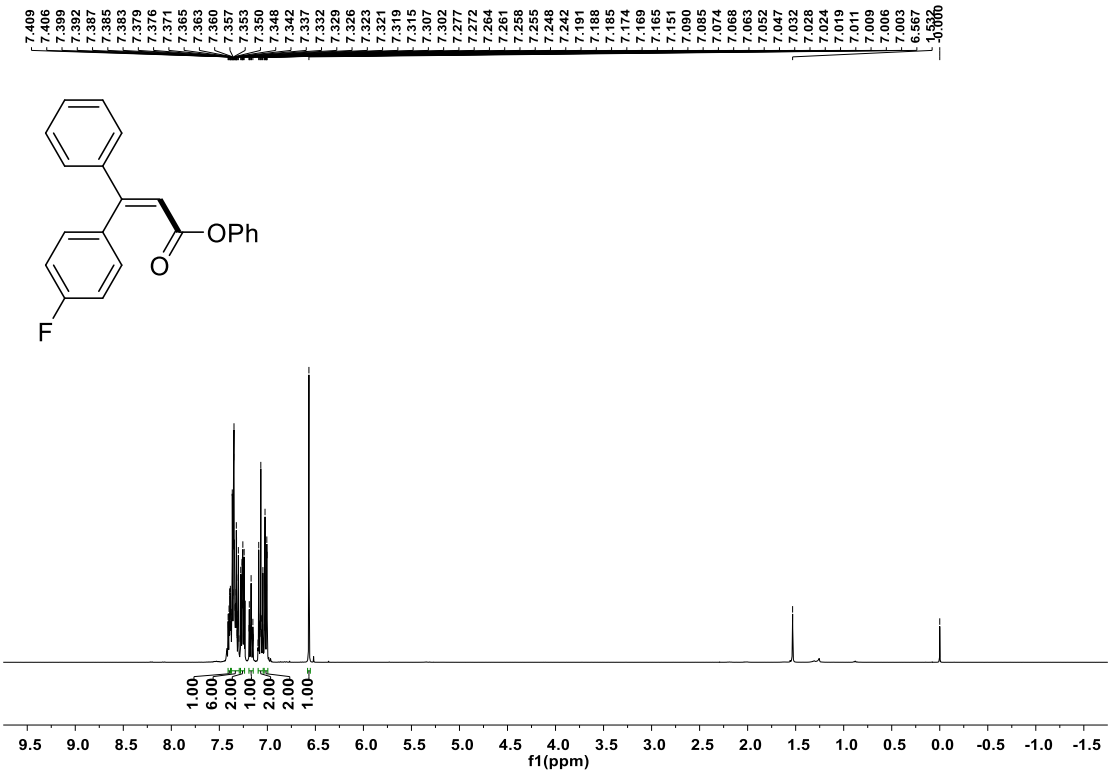
^{1}H NMR of **3q** in $CDCl_3$ (400 MHz)



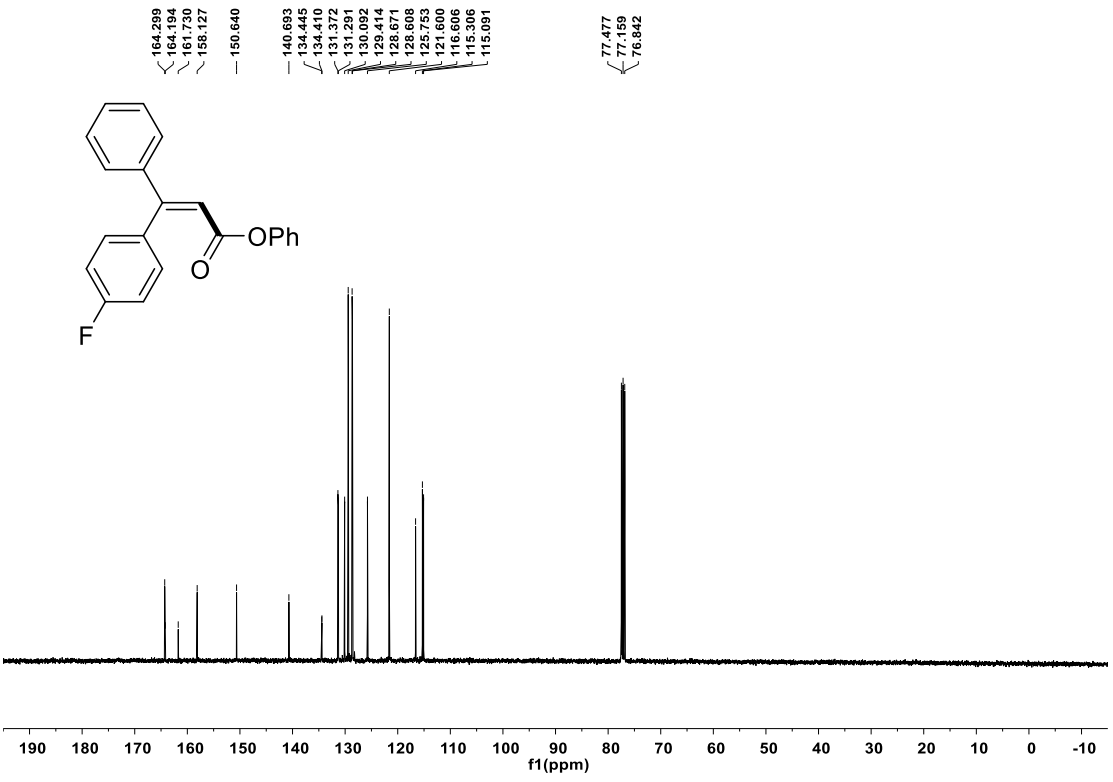
^{13}C NMR of **3q** in $CDCl_3$ (100 MHz)



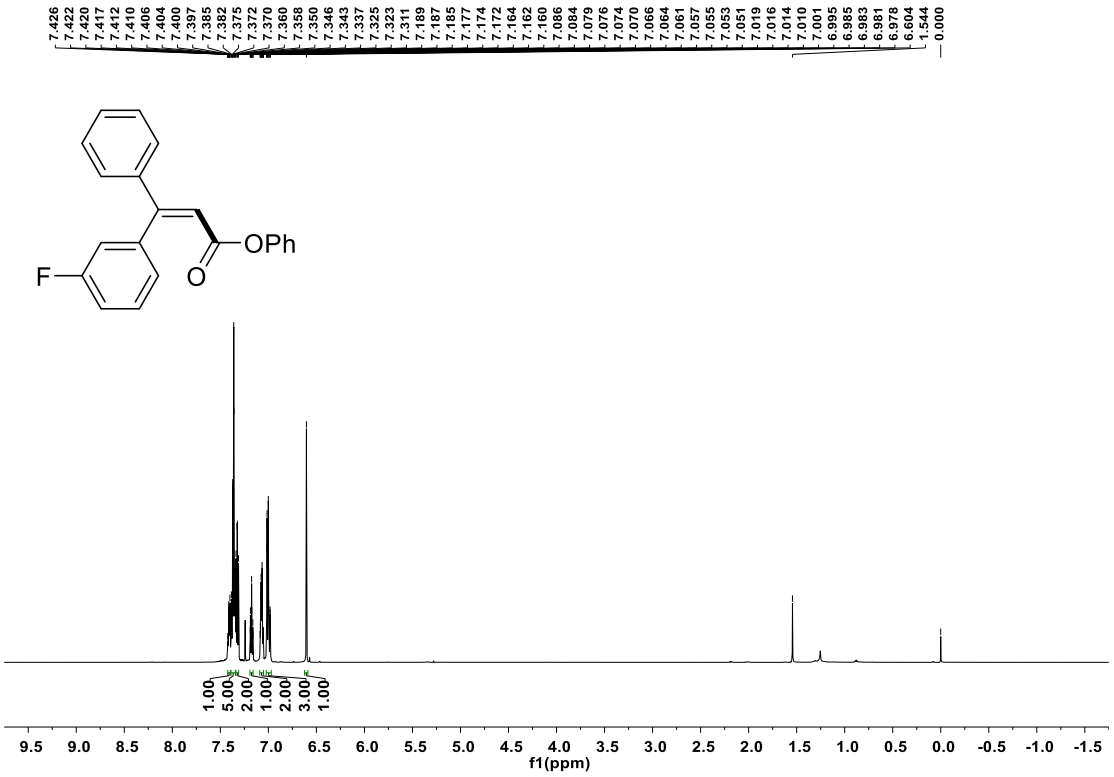
^{1}H NMR of **3r** in $CDCl_3$ (400 MHz)



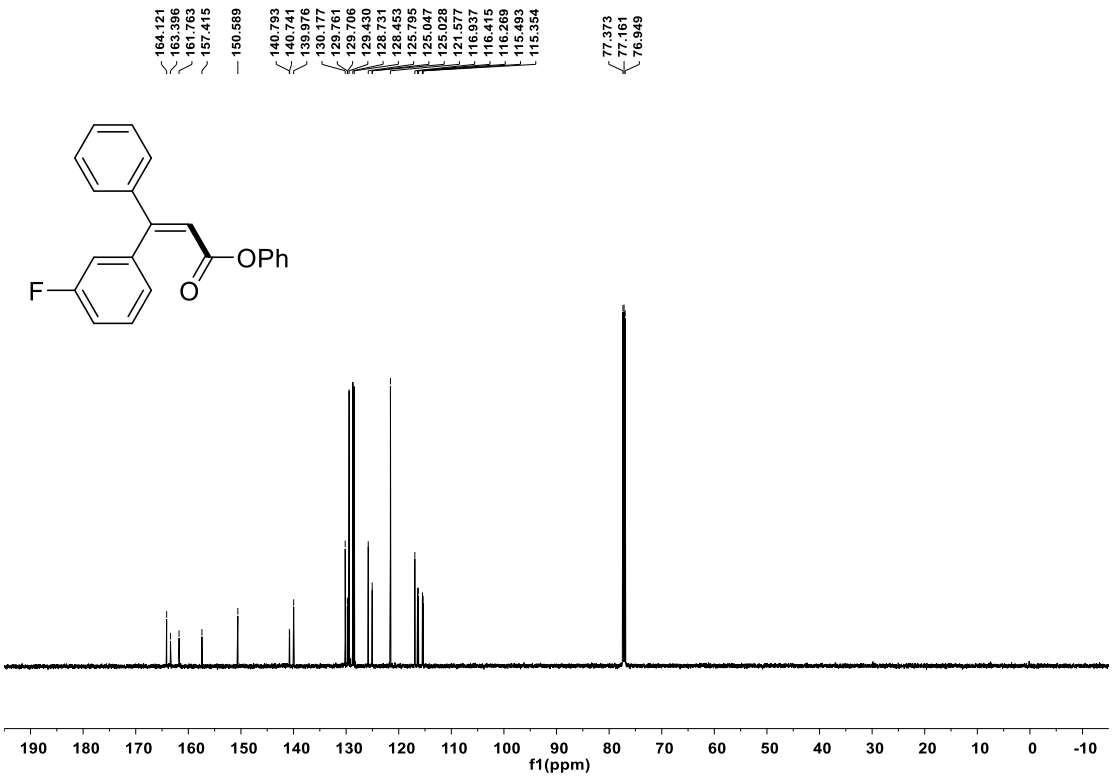
^{13}C NMR of **3r** in $CDCl_3$ (100 MHz)



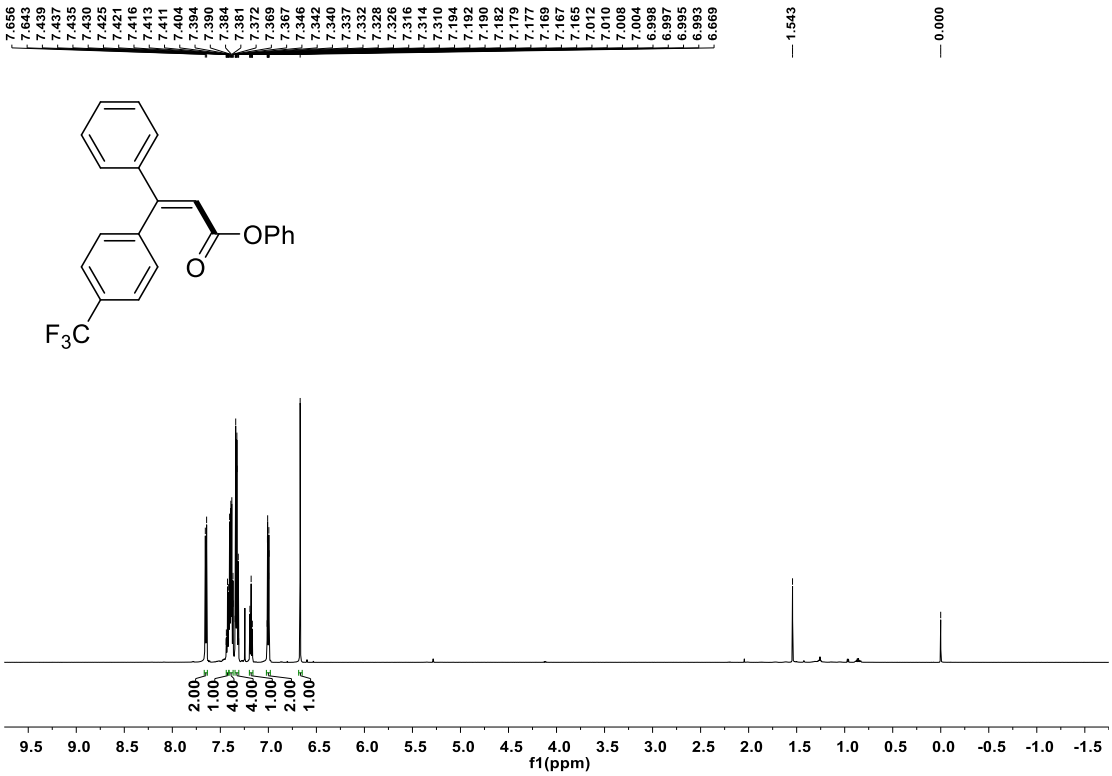
^{1}H NMR of **3s** in $CDCl_3$ (600 MHz)



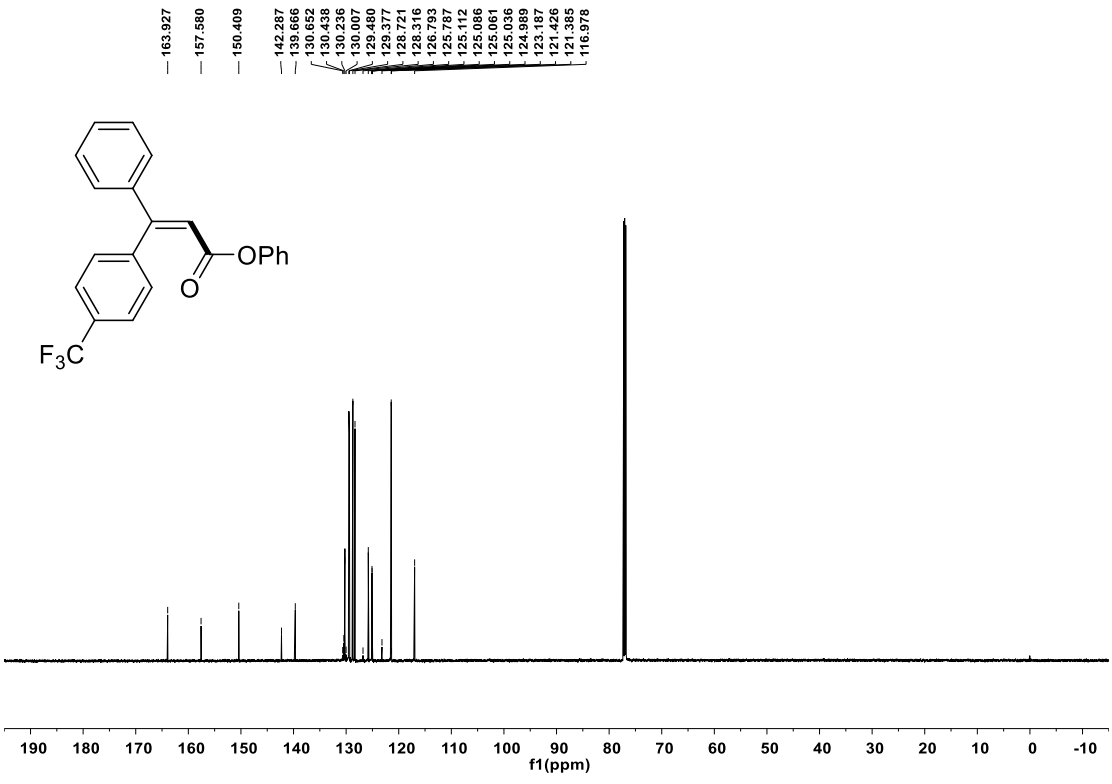
^{13}C NMR of **3s** in $CDCl_3$ (150 MHz)



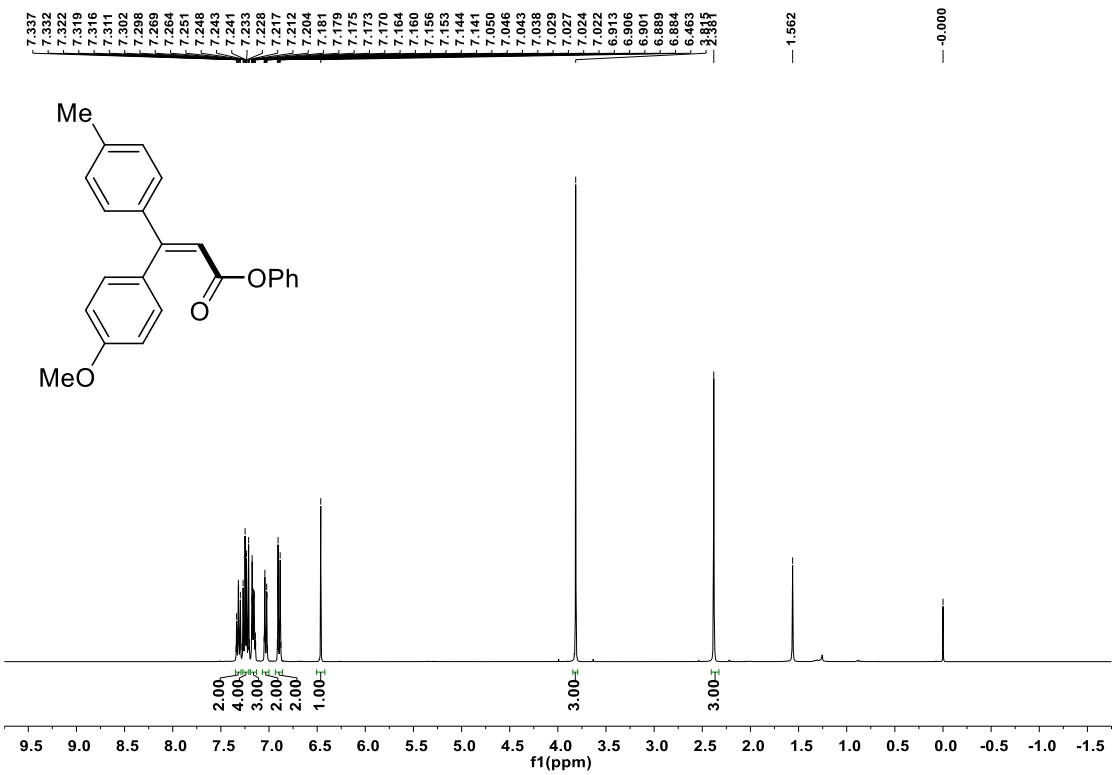
^{1}H NMR of **3t** in $CDCl_3$ (400 MHz)



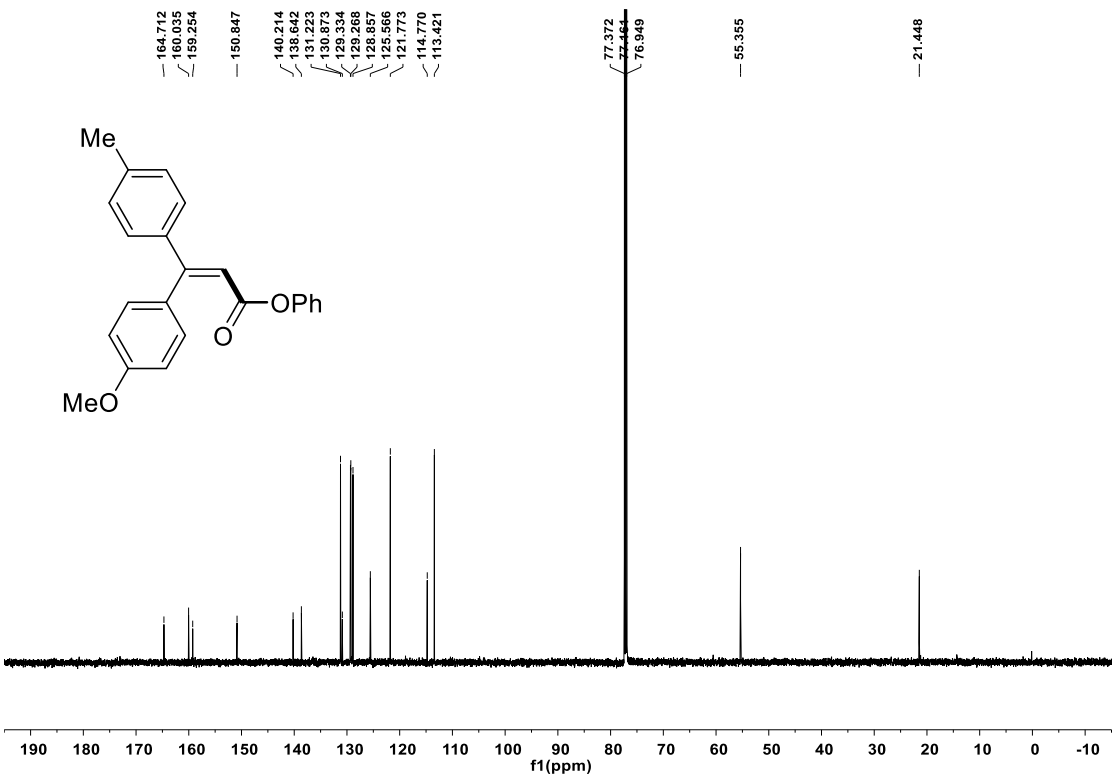
^{13}C NMR of **3t** in $CDCl_3$ (150 MHz)



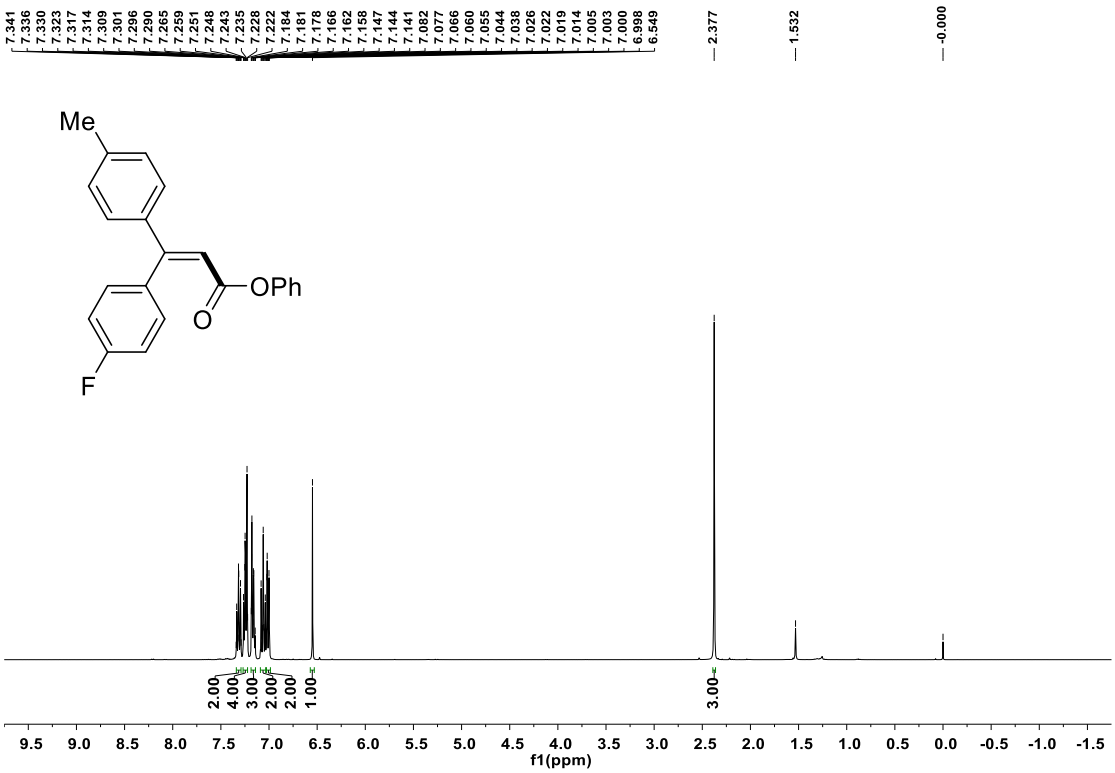
^{1}H NMR of **3u** in $CDCl_3$ (400 MHz)



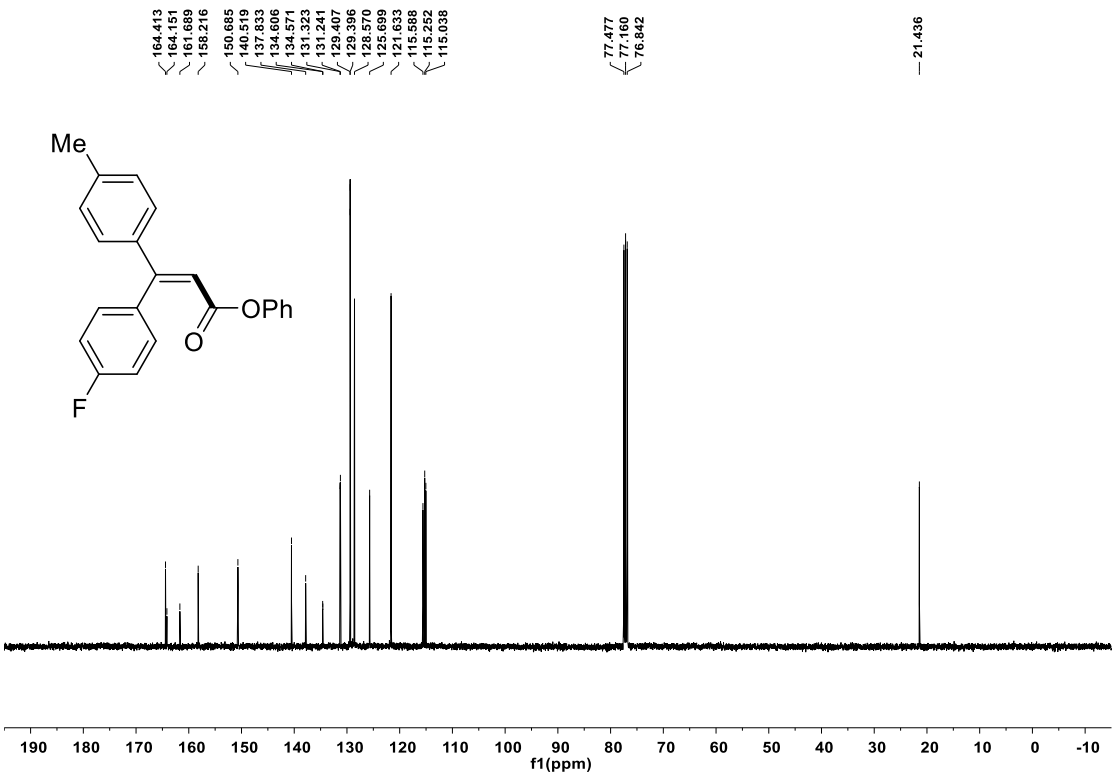
^{13}C NMR of **3u** in $CDCl_3$ (150 MHz)



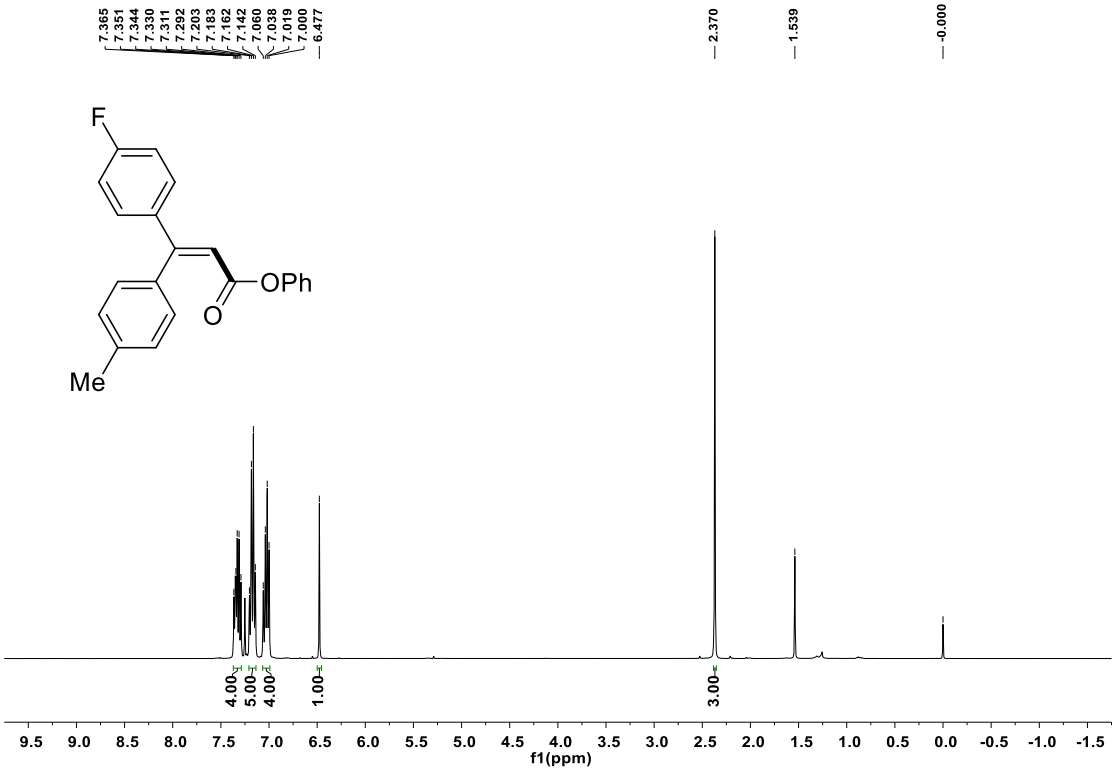
^{1}H NMR of **3v** in $CDCl_3$ (400 MHz)



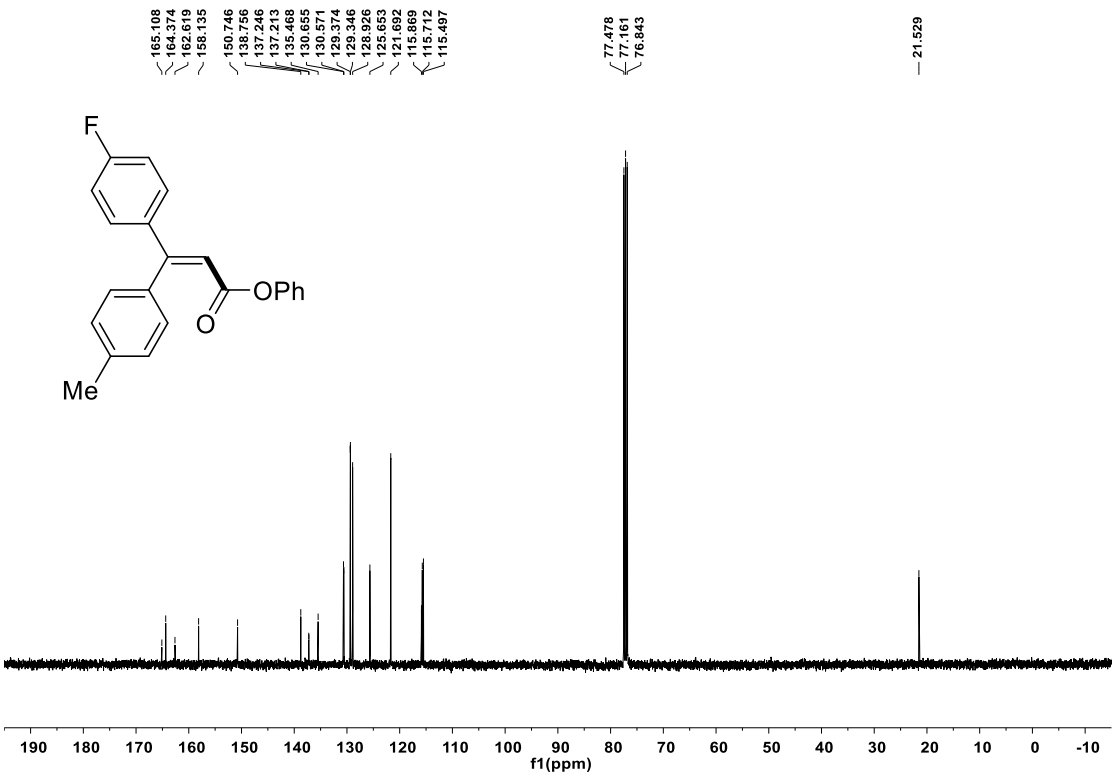
^{13}C NMR of **3v** in $CDCl_3$ (100 MHz)



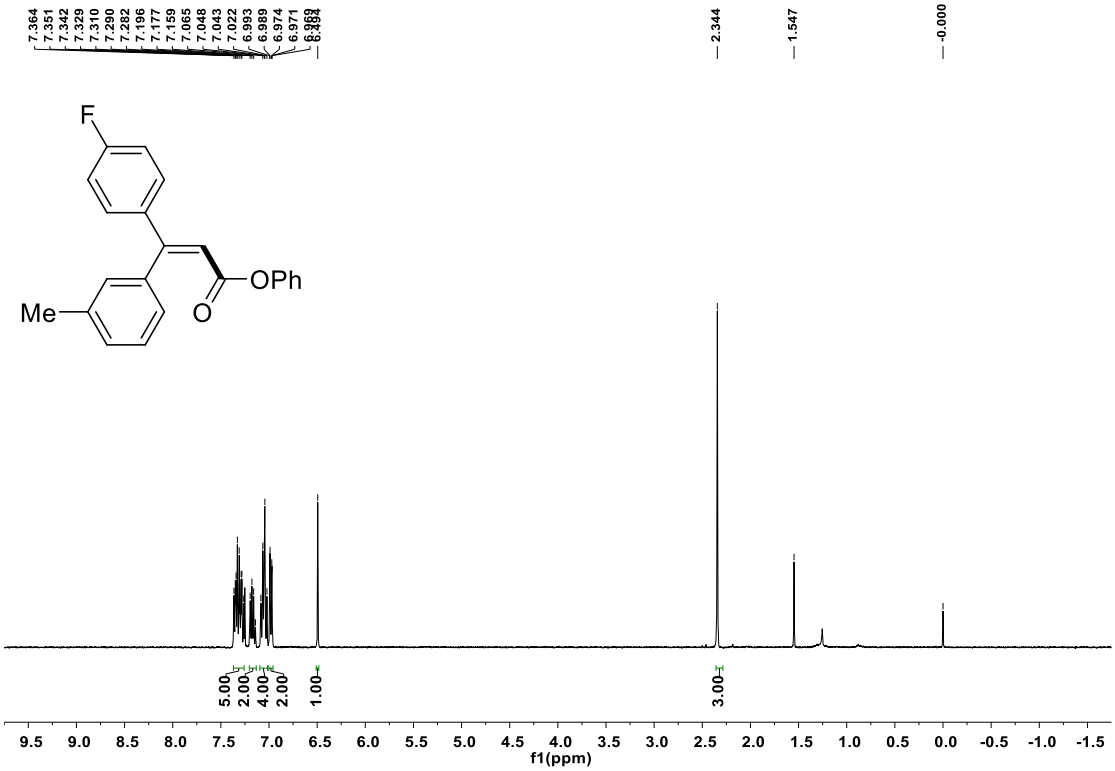
^{1}H NMR of **3w** in $CDCl_3$ (400 MHz)



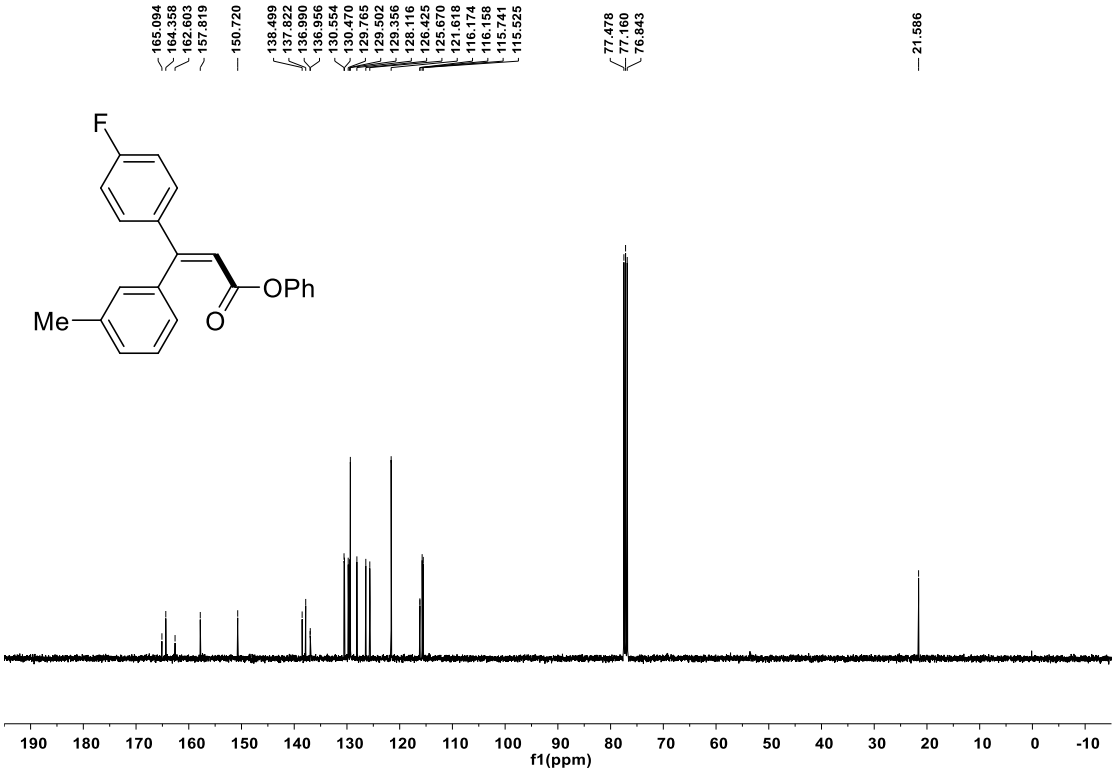
^{13}C NMR of **3w** in $CDCl_3$ (100 MHz)



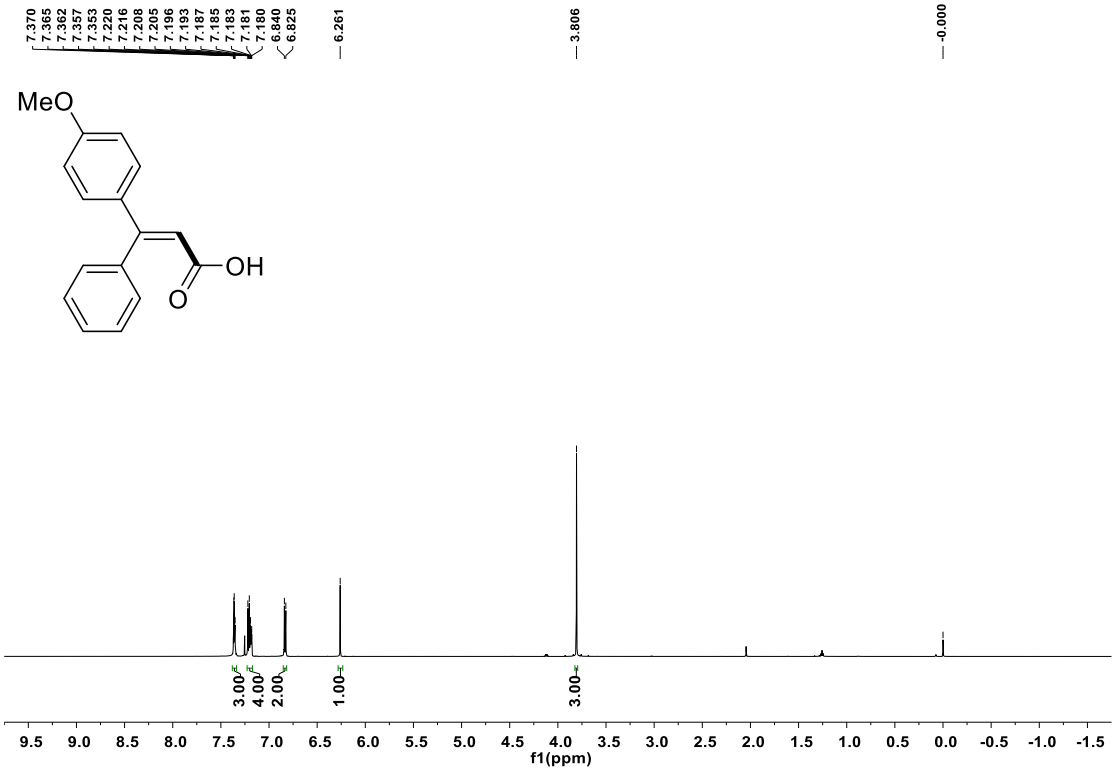
^{1}H NMR of **3x** in $CDCl_3$ (400 MHz)



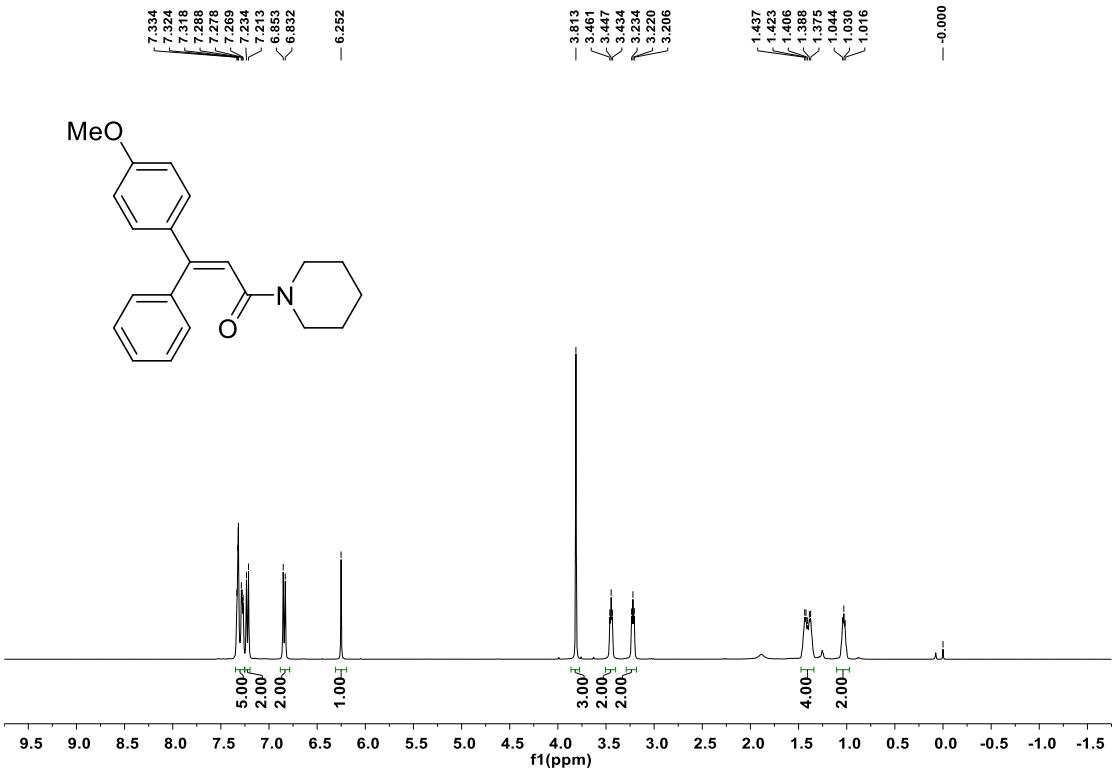
^{13}C NMR of **3x** in $CDCl_3$ (100 MHz)



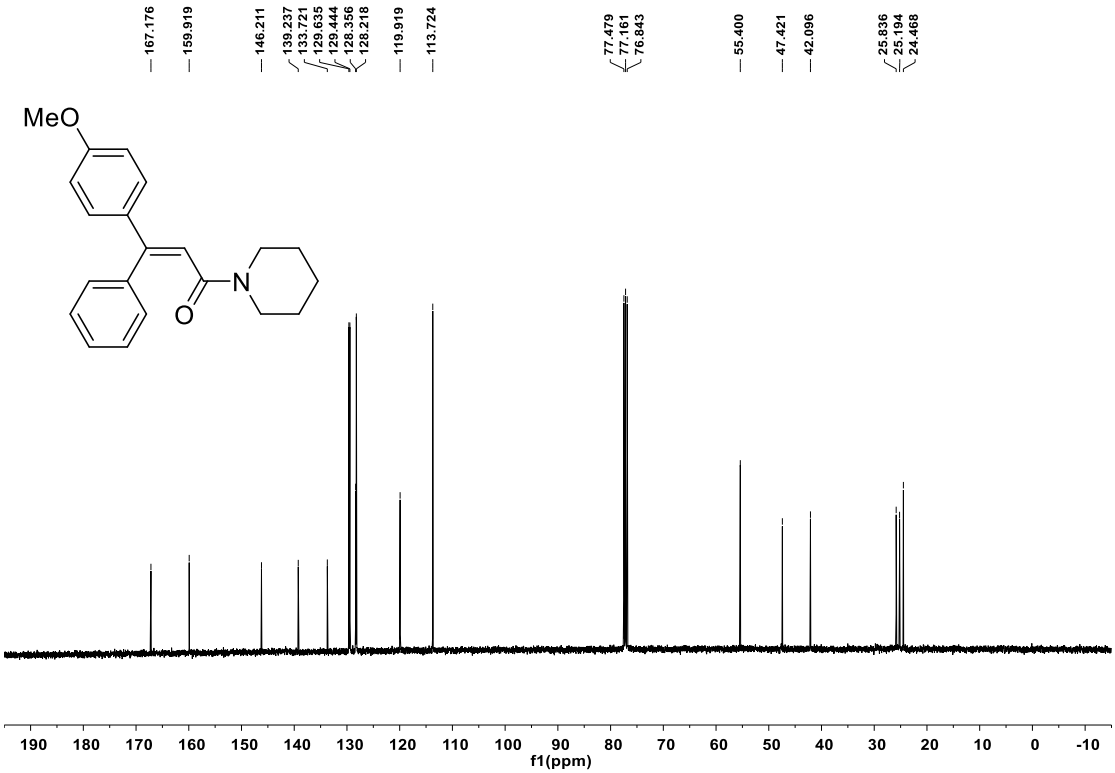
^{1}H NMR of **5** in $CDCl_3$ (600 MHz)



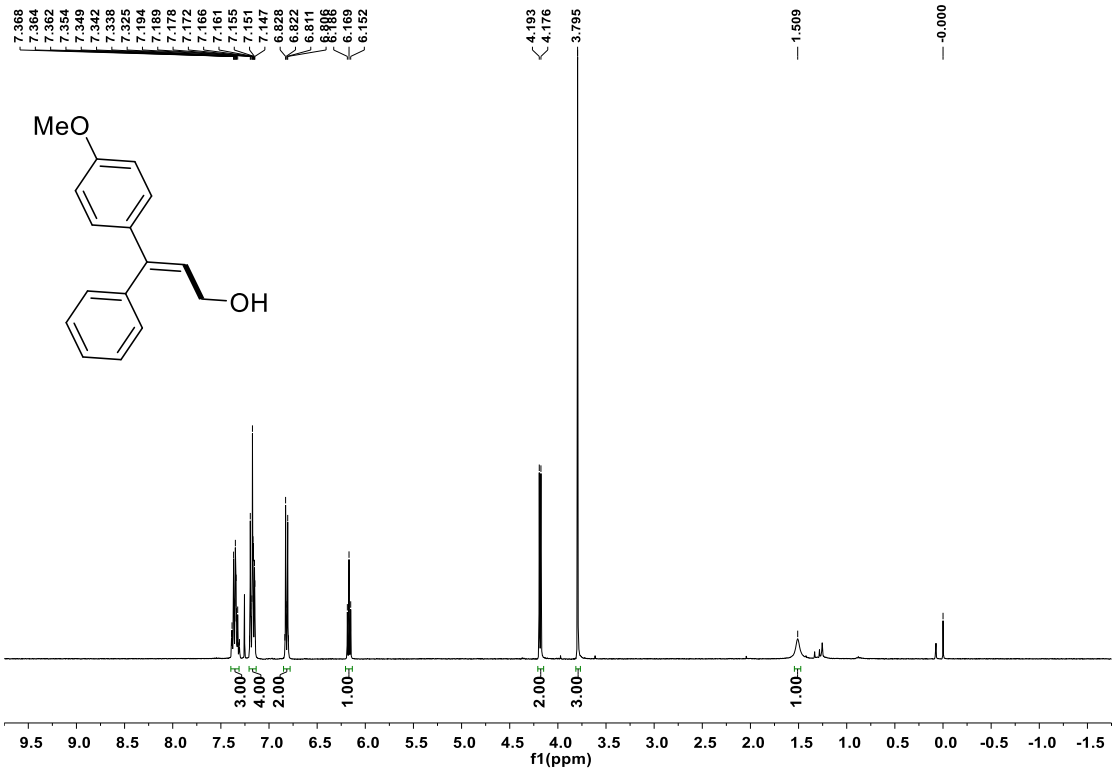
^{1}H NMR of **6** in $CDCl_3$ (400 MHz)



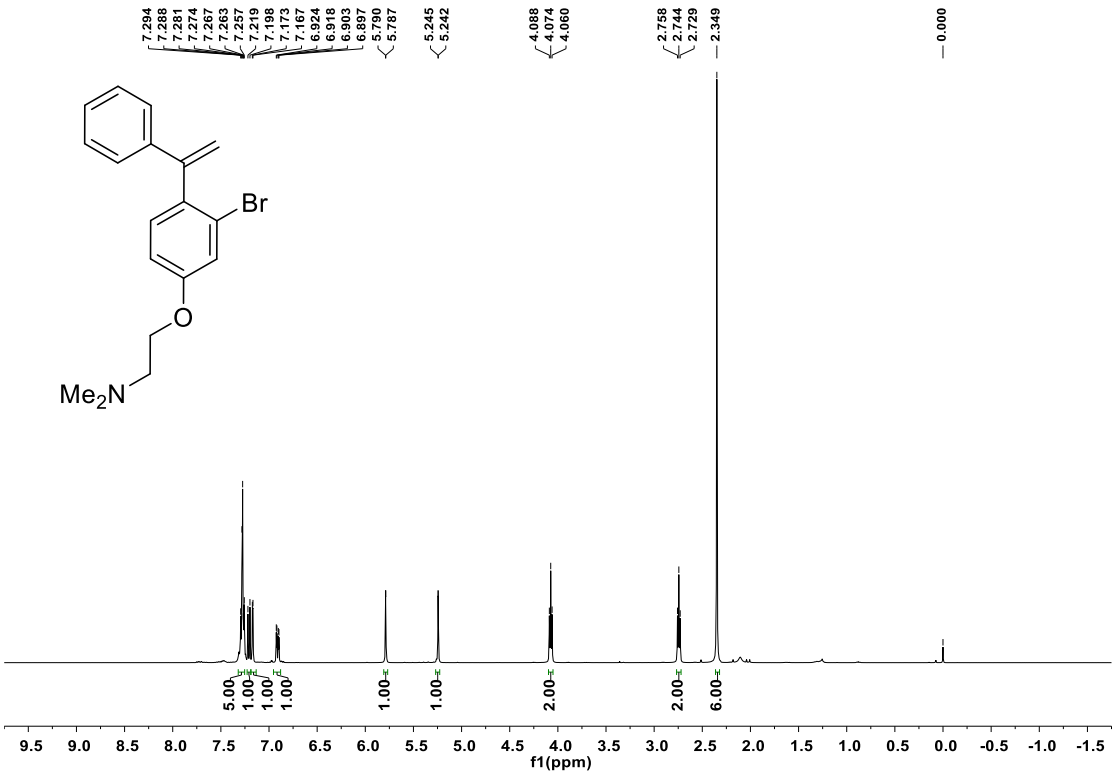
^{13}C NMR of **6** in $CDCl_3$ (100 MHz)



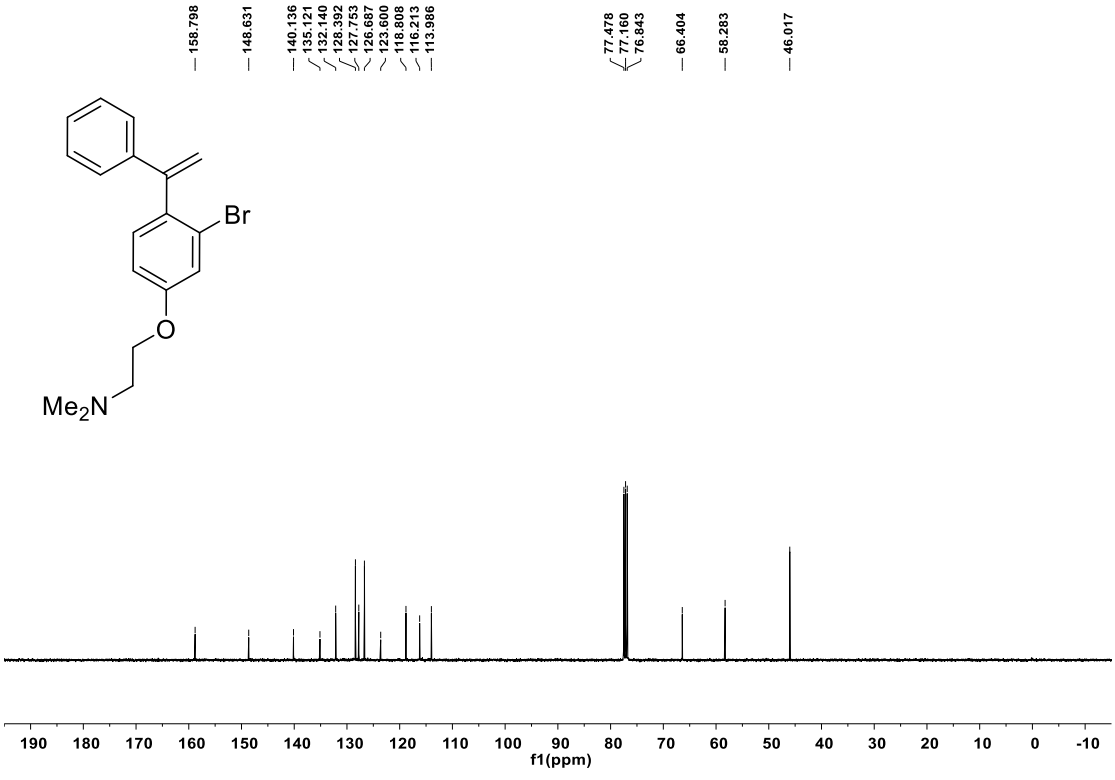
^{1}H NMR of **7** in $CDCl_3$ (400 MHz)



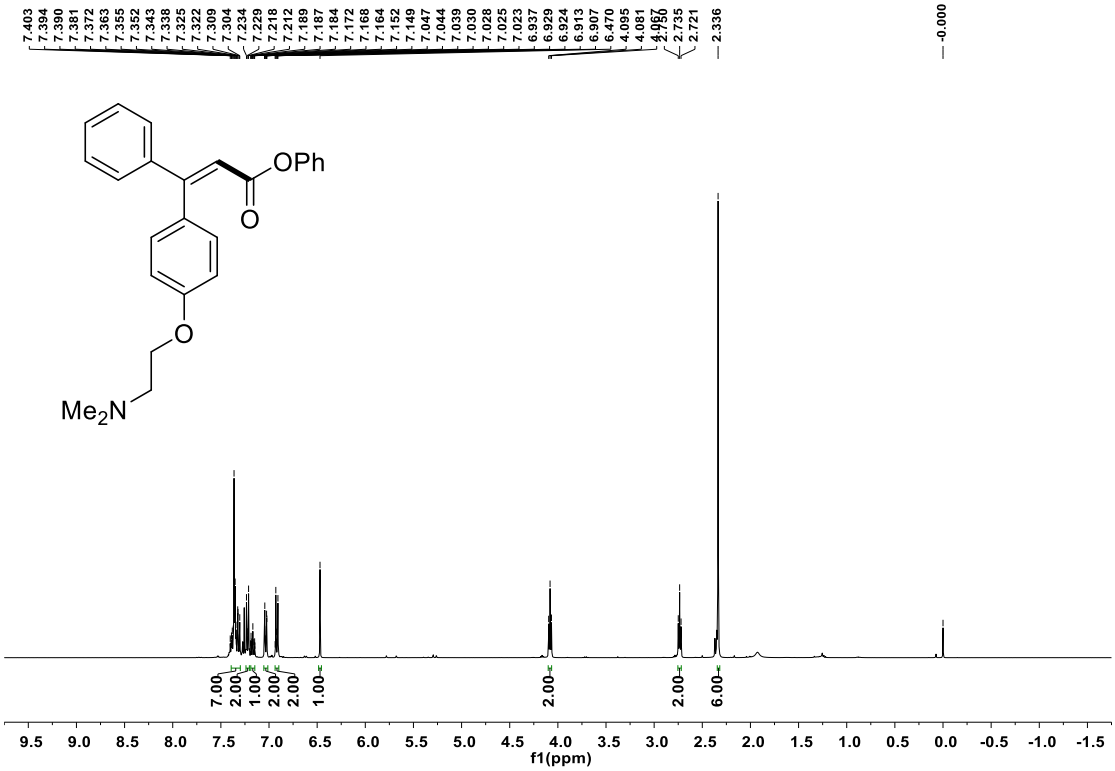
^{1}H NMR of **8** in $CDCl_3$ (400 MHz)



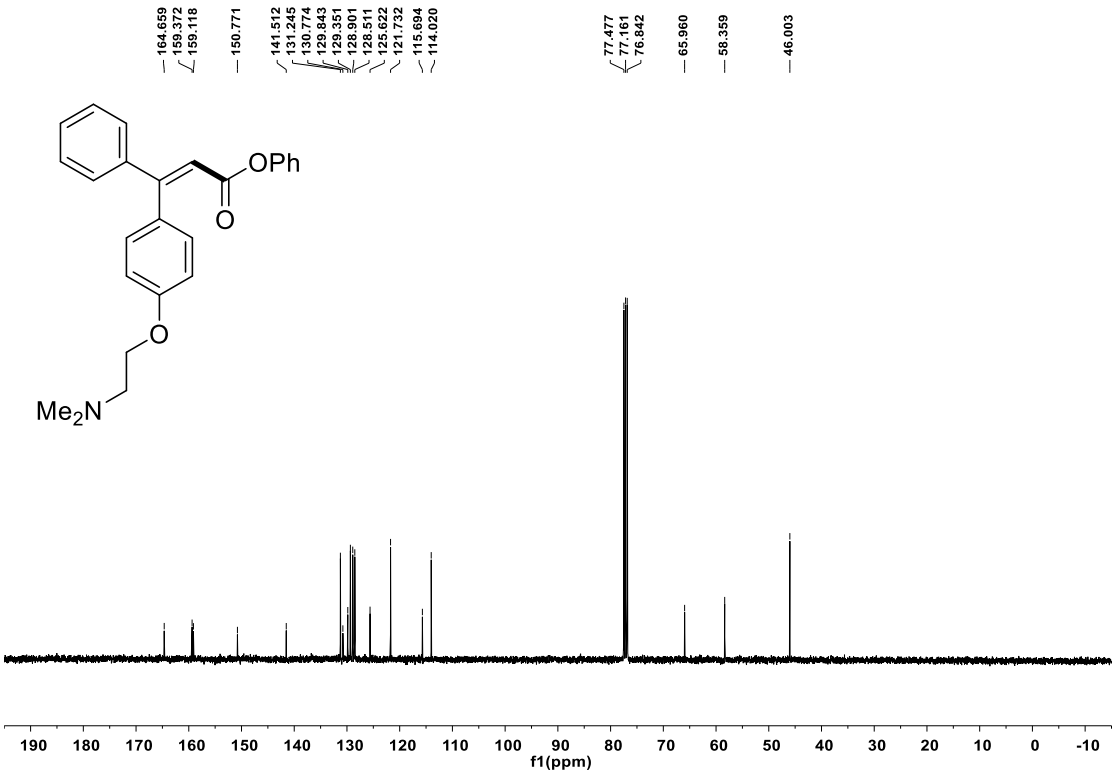
^{13}C NMR of **8** in $CDCl_3$ (100 MHz)



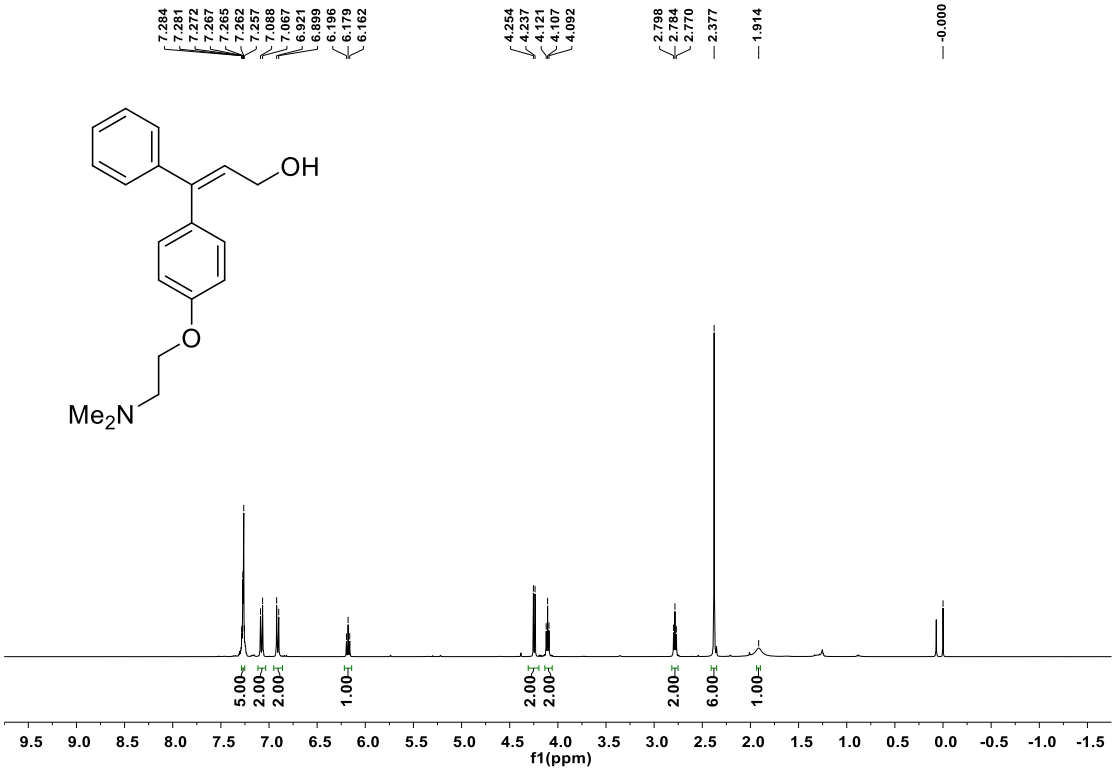
^{1}H NMR of **9** in $CDCl_3$ (400 MHz)



^{13}C NMR of **9** in $CDCl_3$ (100 MHz)



^{1}H NMR of **10** in $CDCl_3$ (400 MHz)



^{13}C NMR of **10** in $CDCl_3$ (100 MHz)