Supporting Information

SO_2F_2 mediated dehydrative cross-coupling of alcohols with electron-deficient olefins in DMSO using Pd-catalyst: one-pot transformation of alcohols to 1,3-dienes

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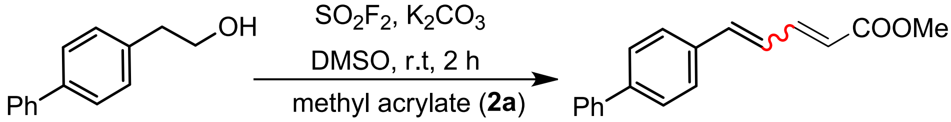
1. General considerations

All reactions were carried out in dried glassware. All reactions were carried out under Ar atmosphere. Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^{1}H), 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^{1}H NMR, 0 ppm) as internal standards. All the yields mentioned were isolated. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet,d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Melting points were measured and uncorrected. Unless otherwise noted, reagents and solvents used in this work were purchasedfrom commercial sources and used as received.

2. Screening the optimized reaction conditions

Table 1. Screening the catalyst loading[a]



1a

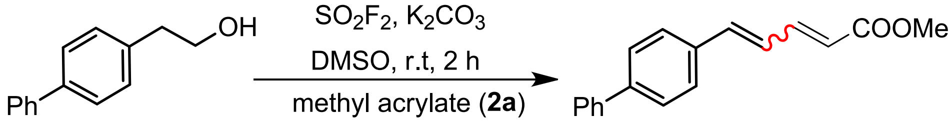
SO_2F_2, K_2CO_3
DMSO, r.t, 2 h
methyl acrylate (**2a**)
$Pd(OAc)_2$ (X mol%)
$NaHCO_3$ (2.0 eq.)
Ar, 50 °C, 24 h

3a

entry	$Pd(OAc)_2$ (mol%)	**3a** yield (%)[b]
1	0.1	0
2	0.5	70
3	**1**	**77**
4	2	74

[a]Reaction condition: a mixture of 2-([1,1-biphenyl]-4-yl)ethanol (**1a**, 1.0 mmol, 1.0 eq.), K_2CO_3 (1.5 mmol, 1.5 eq.), DMSO (2.0 mL) was stirred at room temperature, charged with a SO_2F_2 balloon for 2 h. Then methylacrylate (**2a**, 2.0 mmol, 2.0 eq.), $Pd(OAc)_2$ and $NaHCO_3$ (2.0 mmol, 2.0 eq.) were added into the mixture to react for an additional 24 h under Ar atmosphere (an Ar balloon) at 50 °C. [b]Isolated yields.

Table 2. Screening the reaction tempreture[a]



1a

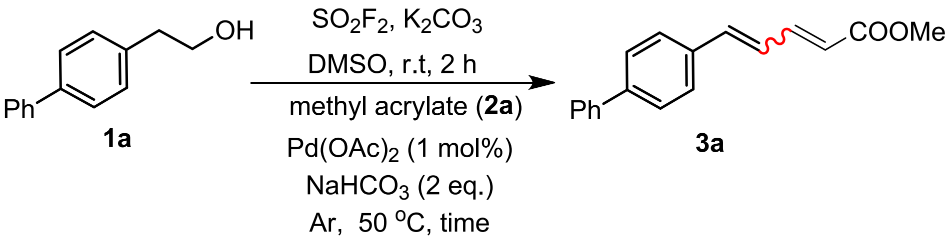
SO_2F_2, K_2CO_3
DMSO, r.t, 2 h
methyl acrylate (**2a**)
$Pd(OAc)_2$ (1 mol%)
$NaHCO_3$ (2 eq.)
Ar, 24 h, T

3a

entry	T (°C)	**3a** yield (%)[b]
1	r.t	0
2	**50**	**77**
3	70	69
4	100	54

[a]Reaction condition: a mixture of 2-([1,1-biphenyl]-4-yl)ethanol (**1a**, 1.0 mmol, 1.0 eq.), K_2CO_3 (1.5 mmol, 1.5 eq.), DMSO (2.0 mL) was stirred at room temperature, charged with a SO_2F_2 balloon for 2 h. Then methylacrylate (**2a**, 2.0 mmol, 2.0 eq.), $Pd(OAc)_2$(1 mol%) and $NaHCO_3$ (2.0 mmol, 2.0 eq.) were added into the mixture to react for an additional 24 h under Ar atmosphere (an Ar balloon) at the corresponding temperature. [b]Isolated yields.

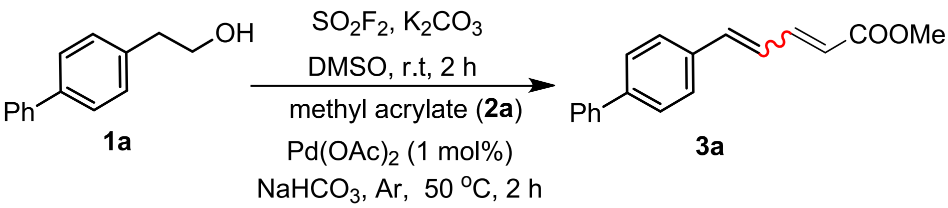
Table 3. Screening the reaction time[a]



entry	time (h)	**3a** yield (%)[b]
1	24	77
2	10	91
3	**2**	**99**
4	1	81
5	0.5	70

[a]Reaction condition: a mixture of 2-([1,1-biphenyl]-4-yl)ethanol (**1a**, 1.0 mmol, 1.0 eq.), K_2CO_3 (1.5 mmol, 1.5 eq.), DMSO (2.0 mL) was stirred at room temperature, charged with a SO_2F_2 balloon for 2 h. Then methylacrylate (**2a**, 2.0 mmol, 2.0 eq.), $Pd(OAc)_2$(1 mol%) and $NaHCO_3$ (2.0 mmol, 2.0 eq.) were added to the mixture to react for an additional 0.5-24 h under Ar atmosphere (an Ar balloon) at 50 °C. [b]Isolated yields.

Table 4. Screening the baseloading[a]

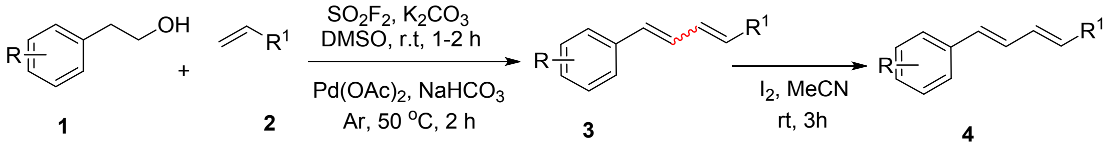


entry	$NaHCO_3$ (eq.)	**3a** yield (%)[b]
1	1	83
2	1.5	90
3	**2**	**99**

[a]Reaction condition: a mixture of 2-([1,1-biphenyl]-4-yl)ethanol (**1a**, 1.0 mmol, 1.0 eq.), K_2CO_3 (1.5 mmol, 1.5 eq.), DMSO (2.0 mL) was stirred at room temperature, charged with a SO_2F_2 balloon for 2 h. Then methylacrylate (**2a**, 2.0 mmol, 2.0 eq.), $Pd(OAc)_2$(1 mol%) and $NaHCO_3$were added to the mixture to react for an additional 2 h under Ar atmosphere (an Ar balloon) at 50 °C. [b]Isolated yields.

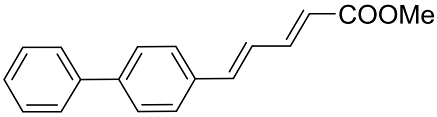
3. General procedure

General procedure for the synthesis of 1,3-diene derivatives.



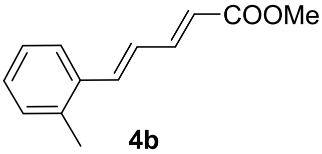
To an oven-dried reaction flask (25 mL) with stirring bar charged with homobenzylic alcohol(**1**, 1.0 mmol, 1.0 eq.), K_2CO_3 (1.5 mmol, 1.5 eq.), the tube was then sealed with a septum, DMSO (2.0 mL) was added through syringe, and SO_2F_2 gas (sulfuryl fluoride) was introduced by needle from a balloon filled with the gas (degassed with SO_2F_2 for 10-30 seconds). The reaction mixture was vigorously stirred at room temperature for 2 h. When the alcohol was consumed (Monitoring by TLC), olefin (**2**, 2.0 mmol, 2.0 eq.),$Pd(OAc)_2$ (1 mol%), $NaHCO_3$ (2.0 mmol, 2.0 eq.) were added into the mixture (degassed with Argon for 10-30 seconds). And then the mixture was allowed to react for an additional 2 h under Argon atmosphere (balloon) at 50 ^{o}C.Subsequently, the mixture was diluted with water (50 mL) and extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (25 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness. The crude residue of compounds**3**(ratio of *E*/*Z* and *E*/*E* about 1:1) was dissolved in MeCN (2.0 mL), I_2 (1.0 mmol) was added and the mixture was allowed to stir at room temperature for 3h.Subsequently, the mixture was diluted with saturated $Na_2S_2O_3$ and water (50 mL) and extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (25 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by silica gel chromatography through gradient elution with EtOAc / Petroleum ether to afford pure products (**4**) as 1-*E*-3-*E*-conjugated-dienes.

4. Product Characterization



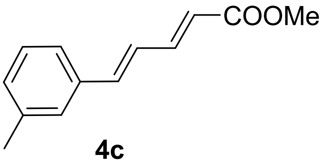
4a

(2*E*,4*E*)-methyl 5-([1,1'-biphenyl]-4-yl)penta-2,4-dienoate (**4a**). White solid (261 mg from 2-([1,1'-biphenyl]-4-yl)ethanol**1a** and methyl acrylate **2a**, isolated yield 99%). M.p. 148-150 °C.The NMR data is identical to that reported in literature.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H),7.54 (d, *J* = 8.5 Hz, 2H),7.51-7.44 (m, 3H),7.37 (t, *J* = 7.5 Hz, 1H),6.93 (d, *J* = 8.5 Hz, 2H),6.02 (d, *J* = 15 Hz, 1H),3.79 (s, 3H).



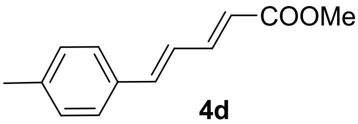
4b

(2*E*,4*E*)-methyl 5-(*o*-tolyl)penta-2,4-dienoate (**4b**). Pale yellow liquid (81 mg from 2-(*o*-tolyl)ethanol**1b** and methyl acrylate **2a**, isolated yield 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ7.56-7.54 (m, 1H), 7.50 (dd, *J*= 15.5Hz, *J*= 11.5 Hz, 1H), 7.22-7.15 (m, 4H), 6.80 (dd, *J* = 15Hz, *J*= 11 Hz, 1H), 6.00 (d, *J* = 15.5 Hz, 1H), 3.78 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 145.3, 138.3, 136.7, 135.0, 130.8, 129.0, 127.3, 126.4, 125.7, 120.8, 51.6, 19.8.



4c

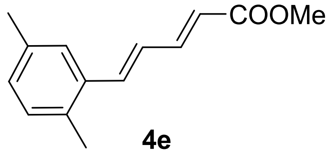
(2*E*,4*E*)-methyl 5-(*m*-tolyl)penta-2,4-dienoate (**4c**). Pale yellow liquid (137 mg from 2-(*m*-tolyl)ethanol**1c** and methyl acrylate **2a**, isolated yield 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.42 (m, 1H), 7.28-7.23 (m, 3H), 7.13 (d, *J* = 6.5 Hz, 1H), 6.87-6.86 (m, 2H), 5.99 (d, *J* = 15.5 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 145.1, 140.9, 138.6, 136.1, 130.1, 128.8, 128.0, 126.2, 124.6, 120.7, 51.7, 21.5.



4d

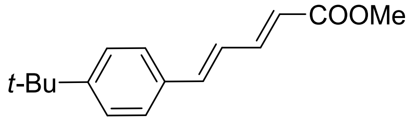
(2*E*,4*E*)-methyl 5-(*p*-tolyl)penta-2,4-dienoate (**4d**). White solid (162 mg from 2-(*p*-tolyl)ethanol**1d** and methyl acrylate **2a**, isolated yield 80%). M.p. 37-38 °C.The NMR data is identical to that reported in literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 15 Hz, *J* =

10 Hz, 1H),7.36 (d, *J* = 8 Hz, 2H),7.16 (d, *J* = 8 Hz, 2H),6.87 (d, *J* = 15.5 Hz, 1H),6.82 (dd, *J* = 15.5 Hz, *J* = 10 Hz, 1H),5.97 (d, *J* = 15 Hz, 1H),3.77 (s, 3H),2.36 (s, 3H).



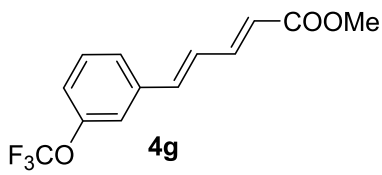
4e

(2*E*,4*E*)-methyl 5-(2,5-dimethylphenyl)penta-2,4-dienoate (**4e**). Pale red liquid (120 mg from 2-(2,5-dimethylphenyl)ethanol **1e** and methyl acrylate **2a**, isolated yield 55%).[1]H NMR (500 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 15 Hz, *J* = 11 Hz, *J* = 0.5 Hz, 1H),7.36 (s, 1H), 7.14 (d, *J* = 15 Hz, 1H),7.08-7.02 (m, 2H),6.80 (dd, *J* = 15.5 Hz, *J* = 11 Hz, 1H),6.00 (d, *J* = 15.5 Hz, 1H),3.78 (s, 3H),2.35 (s, 3H),2.33 (s, 3H).[13]C NMR (126 MHz, $CDCl_3$) δ 167.7, 145.4, 138.5, 135.8, 134.7, 133.7, 130.7, 129.9, 127.0, 126.3, 120.6, 51.7, 21.1, 19.3.



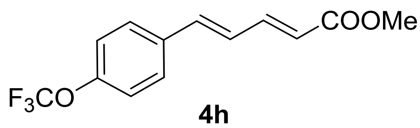
4f

(2*E*,4*E*)-methyl 5-(4-(*tert*-butyl)phenyl)penta-2,4-dienoate (**4f**). Pale yellow solid (151 mg from 2-(4-(*tert*-butyl)phenyl)ethanol **1f** and methyl acrylate **2a**, isolated yield 62%). M.p. 88-90°C.[1]H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 15.5 Hz, *J* = 10.5 Hz, 1H), 7.43-7.37 (m, 4H), 6.90 (d, *J* = 15.5 Hz, 1H),6.84 (dd, *J* = 15.5 Hz, *J* = 10 Hz, 1H),5.98 (d, *J* = 15 Hz, 1H),3.77 (s, 3H),1.33 (s, 9H). [13]C NMR (126 MHz, $CDCl_3$) δ 167.7, 152.7, 145.3, 140.7, 133.4, 127.2, 125.9, 125.6, 120.4, 51.6, 34.9, 31.3.



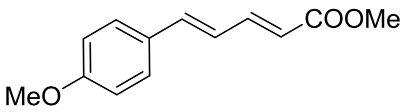
4g

(2*E*,4*E*)-methyl 5-(3-(trifluoromethoxy)phenyl)penta-2,4-dienoate (**4g**). Yellowliquid (163 mg from 2-(3-(trifluoromethoxy)phenyl)ethanol **1g** and methyl acrylate **2a**, isolated yield 60%).[1]H NMR (500 MHz, $CDCl_3$) δ 7.43 (ddd, *J* = 15 Hz, *J* = 7 Hz,*J* = 3 Hz, 1H),7.38-7.37 (m, 2H),7.30 (s, 1H), 7.16-7.14 (m, 1H),6.88-6.86 (m, 2H),6.04 (d, *J* = 15.5 Hz, 1H),3.78 (s, 3H). [13]C NMR (126 MHz, $CDCl_3$) δ 167.4, 149.9, 144.1, 138.7, 138.3, 130.3, 128.0, 125.7, 122.3, 121.6, 121.3, 119.4, 51.8.



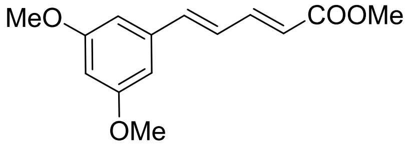
4h

(2*E*,4*E*)-methyl 5-(4-(trifluoromethoxy)phenyl)penta-2,4-dienoate (**4h**). White solid (175 mg from 2-(4-(trifluoromethoxy)phenyl)ethanol **1h** and methyl acrylate **2a**, isolated yield 64%). M.p. 74-76 °C.^{1}H NMR (500 MHz,$CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H),7.43 (dd, *J* = 15.5 Hz, *J* = 9.5 Hz, 1H),7.19 (d, *J* = 8 Hz, 2H),6.89-6.80 (m, 2H),6.02 (d, *J* = 15 Hz, 1H),3.77 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 149.6, 149.6, 144.4, 138.7, 134.8, 128.6, 127.2, 121.7, 121.3, 51.7.



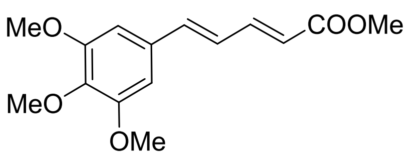
4i

(2*E*,4*E*)-methyl 5-(4-methoxyphenyl)penta-2,4-dienoate (**4i**). Pale yellow solid (157 mg from 2-(4-methoxyphenyl)ethanol **1i** and methyl acrylate **2a**, isolated yield 72%). M.p. 116-118 °C.The NMR data is identical to that reported in literature.[21] ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.46-7.39 (m, 3H), 6.89-6.83 (m, 3H), 6.74(dd, *J* = 15.5 Hz, *J* = 10.5 Hz, 1H), 5.94 (d, *J* = 15 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H).



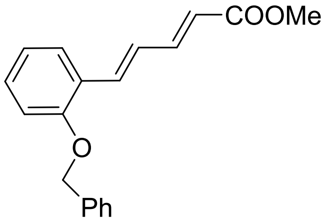
4j

(2*E*,4*E*)-methyl 5-(3,5-dimethoxyphenyl)penta-2,4-dienoate (**4j**). Pale yellow solid (149 mg from 2-(3,5-dimethoxyphenyl)ethanol **1j** and methyl acrylate **2a**, isolated yield 60%). M.p. 96-98 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (ddd, *J* = 15 Hz, *J* = 6.5 Hz, *J* = 3.5 Hz, 1H),6.84-6.83 (m, 2H),6.61 (d, *J* = 2 Hz, 2H),6.43 (t, *J* = 2 Hz, 1H),6.00 (d, *J* = 15.5 Hz, 1H),3.81 (s, 6H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 161.2, 144.7, 140.6, 138.1, 126.8, 121.2, 105.4, 101.6, 55.5, 51.7.



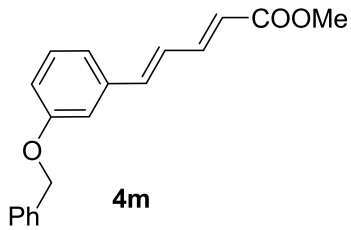
4k

(2*E*,4*E*)-methyl 5-(3,4,5-trimethoxyphenyl)penta-2,4-dienoate (**4k**). Yellowliquid (139 mg from 2-(3,4,5-trimethoxyphenyl)ethanol **1k** and methyl acrylate **2a**, isolated yield 50%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 15.5 Hz, *J* = 10 Hz, 1H),6.84-6.78 (m, 2H),6.68 (s, 2H), 5.99 (d, *J* = 15.5 Hz, 1H),3.89 (s, 6H),3.87 (s, 3H),3.77 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 153.6, 144.8, 140.6, 139.4, 131.8, 125.8, 120.7, 104.6, 61.1, 56.3, 51.7.



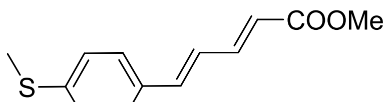
4l

(2*E*,4*E*)-methyl 5-(2-(benzyloxy)phenyl)penta-2,4-dienoate (**4l**). Yellowliquid (182 mg from 2-(2-(benzyloxy)phenyl)ethanol **1l** and methyl acrylate **2a**, isolated yield 62%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.5 Hz, *J* = 1 Hz, 1H), 7.41-7.36 (m, 5H),7.33-7.29 (m, 2H),7.22-7.20 (m, 1H), 6.94-6.90 (m, 3H), 5.89 (d, *J* = 15.5 Hz, 1H),5.08 (s, 2H),3.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 156.8, 146.0, 136.8, 135.8, 130.3, 128.8, 128.2, 127.6, 127.5, 127.0, 125.5, 121.2, 120.2, 112.7, 70.5, 51.6.



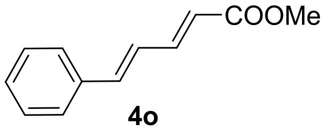
4m

(2*E*,4*E*)-methyl 5-(3-(benzyloxy)phenyl)penta-2,4-dienoate (**4m**). White solid (186 mg from 2-(3-(benzyloxy)phenyl)ethanol **1m** and methyl acrylate **2a**, isolated yield 63%). M.p. 89-91 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.37 (m, 5H),7.34-7.32 (m, 1H),7.26-7.25 (m, 1H),7.07-7.06 (m, 2H),6.94-6.92 (m, 1H),6.85-6.84 (m, 2H),5.99 (d, *J* = 15 Hz, 1H),5.08 (s, 2H), 3.77 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 159.3, 144.8, 140.5, 137.6, 136.9, 130.0, 128.8, 128.2, 127.6, 126.7, 121.1, 120.3, 115.8, 113.5, 70.2, 51.7.



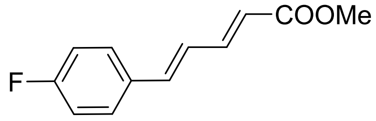
4n

(2*E*,4*E*)-methyl 5-(4-(methylthio)phenyl)penta-2,4-dienoate (**4n**). White solid (180 mg from 2-(4-(methylthio)phenyl)ethanol **1n** and methyl acrylate **2a**, isolated yield 77%). M.p. 101-103 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (ddd, *J* = 15 Hz, *J* = 8 Hz,*J* = 2 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H),7.21 (d, *J* = 8.5 Hz, 2H), 6.84-6.82 (m, 2H), 5.97 (d, *J* = 15 Hz, 1H),3.77 (s, 3H),2.49 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 145.0, 140.3, 140.1, 132.9, 127.7, 126.4, 125.6, 120.5, 51.7, 15.5.



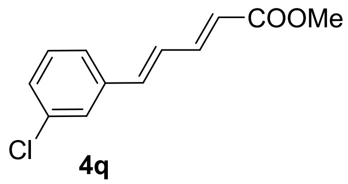
4o

(2*E*,4*E*)-methyl 5-phenylpenta-2,4-dienoate (**4o**). White solid (133 mg from 2-phenylethanol **1o** and methyl acrylate **2a**, isolated yield 71%). M.p. 60-62 ^{o}C.The NMR data is identical to that reported in literature.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.43 (m, 3H),7.36 (t, *J* = 7 Hz, 2H),7.30 (t, *J* = 7 Hz, 1H),6.92-6.84 (m, 2H), 6.00 (d, *J* = 15 Hz, 1H),3.77 (s, 3H).



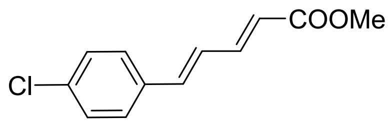
4p

(2*E*,4*E*)-methyl 5-(4-fluorophenyl)penta-2,4-dienoate (**4p**). White solid (140 mg from 2-(4-fluorophenyl)ethanol **1p** and methyl acrylate **2a**, isolated yield 68%). M.p. 90-92 ^{o}C.The NMR data is identical to that reported in literature.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 3H),7.04 (t, *J* = 9 Hz, 2H),6.85 (d, *J* = 15.5 Hz, 1H),6.78 (dd, *J* = 15.5 Hz,*J* = 10.5 Hz, 1H),5.98 (d, *J* = 15 Hz, 1H), 3.77 (s, 3H).



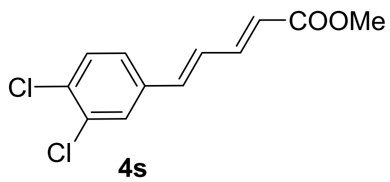
4q

(2*E*,4*E*)-methyl 5-(3-chlorophenyl)penta-2,4-dienoate (**4q**). Red solid (115 mg from 2-(3-chlorophenyl)ethanol **1q** and methyl acrylate **2a**, isolated yield 52%). M.p. 49-51 ^{o}C.The NMR data is identical to that reported in literature.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.33-7.30 (m, 1H),7.28-7.27 (m, 2H),6.86 (dd, *J* = 15.5 Hz,*J* = 10 Hz, 1H),6.81 (d, *J* = 15.5 Hz, 1H),6.02 (d, *J* = 15.5 Hz, 1H), 3.77 (s, 3H).



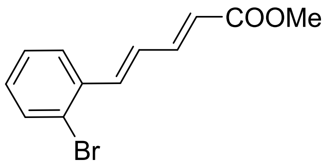
4r

(2*E*,4*E*)-methyl 5-(4-chlorophenyl)penta-2,4-dienoate (**4r**). White solid (156 mg from 2-(4-chlorophenyl)ethanol **1r** and methyl acrylate **2a**, isolated yield 70%). M.p. 122-124 ^{o}C.The NMR data is identical to that reported in literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ7.45-7.41 (m,1H), 7.38 (dt, *J* = 10.5 Hz, *J* = 4 Hz, 2H), 7.32 (dt, *J* = 9 Hz, *J* = 2 Hz, 2H), 6.84-6.83 (m, 2H), 6.00 (d, *J* = 15.5 Hz, 1H), 3.77 (s, 3H).



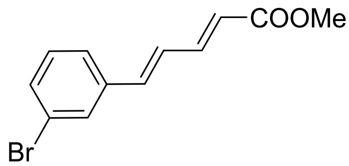
4s

(2*E*,4*E*)-methyl 5-(3,4-dichlorophenyl)penta-2,4-dienoate (**4s**). Pale yellow solid (136 mg from 2-(3,4-dichlorophenyl)ethanol **1s** and methyl acrylate **2a**, isolated yield 53%). M.p. 114-115 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2 Hz, 1H),7.43-7.38 (m, 2H), 7.28 (d, *J* = 2 Hz, 1H),6.84(dd, *J* = 15.5 Hz, *J* = 10.5 Hz, 1H), 6.77 (d, *J* = 16 Hz, 1H), 6.03 (d, *J* = 15.5 Hz, 1H),3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 144.0, 137.7, 136.2, 133.2, 132.9, 130.9, 128.8, 128.0, 126.3, 122.4, 51.8.



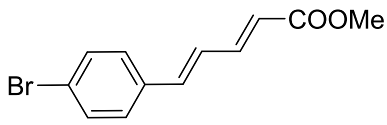
4t

(2*E*,4*E*)-methyl 5-(2-bromophenyl)penta-2,4-dienoate (**4t**). Red solid (155 mg from 2-(2-bromophenyl)ethanol **1t** and methyl acrylate **2a**, isolated yield 58%). M.p. 60-62 °C.The NMR data is identical to that reported in literature.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.36-7.33 (m, 2H),7.31-7.29 (m, 1H), 6.88-6.83 (m, 2H), 5.99 (d, *J* = 15 Hz, 1H), 3.76 (s, 3H).



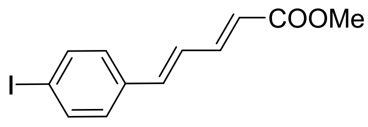
4u

(2*E*,4*E*)-methyl 5-(3-bromophenyl)penta-2,4-dienoate (**4u**). Redliquid (160 mg from 2-(3-bromophenyl)ethanol **1u** and methyl acrylate **2a**, isolated yield 60%). The NMR data is identical to that reported in literature.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H),7.35 (t, *J* = 7 Hz, 2H),7.32-7.29 (m, 1H),6.89-6.81 (m, 2H),6.00 (d, *J* = 15.5 Hz, 1H),3.77 (s, 3H).



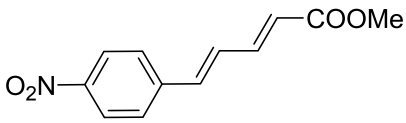
4v

(2*E*,4*E*)-methyl 5-(4-bromophenyl)penta-2,4-dienoate (**4v**). White solid (165 mg from 2-(4-bromophenyl)ethanol **1v** and methyl acrylate **2a**, isolated yield 62%). M.p. 136-138 °C.The NMR data is identical to that reported in literature.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H),7.41 (ddd, *J* = 15 Hz, *J* = 8.5 Hz,*J* = 1 Hz, 1H),7.31 (d, *J* = 8.5 Hz, 2H),6.87-6.79 (m, 2H),6.00 (d, *J* = 15.5 Hz, 1H),3.77 (s, 3H).



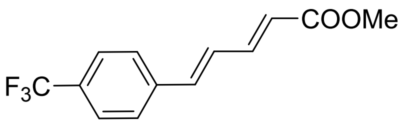
4w

(2*E*,4*E*)-methyl 5-(4-iodophenyl)penta-2,4-dienoate (**4w**). White solid (172 mg from 2-(4-iodophenyl)ethanol **1w** and methyl acrylate **2a**, isolated yield 55%). M.p. 66-68 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H),7.35 (t, *J* = 7 Hz, 2H),7.30 (t, *J* = 7 Hz, 1H),6.92-6.84 (m, 2H),6.00 (d, *J* = 15 Hz, 1H),3.77(s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 144.9, 140.7, 136.1, 129.2, 128.9, 127.3, 126.3, 120.9, 51.6.



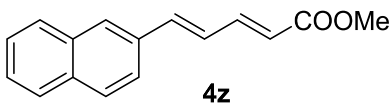
4x

(2*E*,4*E*)-methyl 5-(4-nitrophenyl)penta-2,4-dienoate (**4x**). Yellow solid (116 mg from 2-(4-nitrophenyl)ethanol **1x** and methyl acrylate **2a**, isolated yield 50%). M.p. 160-162 °C.The NMR data is identical to that reported in literature.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 2H),7.59 (d, *J* = 8.5 Hz, 2H),7.45 (dd, *J* = 15 Hz, *J* = 10.5 Hz, 1H),7.00 (dd, *J* = 15.5 Hz, *J* = 10.5 Hz, 1H), 6.93 (d, *J* = 15.5 Hz, 1H),6.11 (d, *J* = 15.5 Hz, 1H),3.79 (s, 3H).



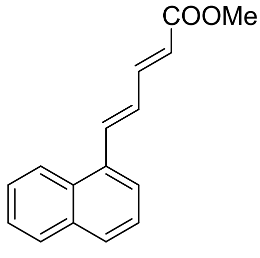
4y

(2*E*,4*E*)-methyl 5-(4-(trifluoromethyl)phenyl)penta-2,4-dienoate (**4y**). Pale yellow solid (159 mg from 2-(4-(trifluoromethyl)phenyl)ethanol **1y** and methyl acrylate **2a**, isolated yield 62%). M.p. 108-110 °C.The NMR data is identical to that reported in literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H),7.55 (d, *J* = 8.5 Hz, 2H), 7.45 (ddd, *J* = 15.5 Hz, *J* = 9 Hz,*J* = 1.5 Hz, 1H),6.97-6.89 (m, 2H),6.06 (d, *J* = 15 Hz, 1H),3.78 (s, 3H).



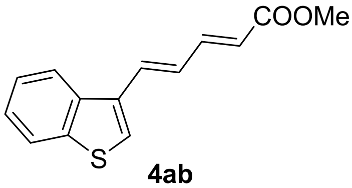
4z

(2*E*,4*E*)-methyl 5-(naphthalen-2-yl)penta-2,4-dienoate (**4z**). White solid (175 mg from 2-(naphthalen-2-yl)ethanol **1z** and methyl acrylate **2a**, isolated yield 74%). M.p. 100-101 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 4H),7.65 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H),7.54-7.48 (m, 3H), 7.07 (d, *J* = 15.5 Hz, 1H),6.99 (dd, *J* = 15.5 Hz, *J* = 10.5 Hz, 1H),6.04 (d, *J* = 15 Hz, 1H),3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 145.0, 140.8, 133.8, 133.7, 133.6, 128.7, 128.4, 128.3, 127.9, 126.8, 126.7, 126.6, 123.5, 121.0, 51.7.



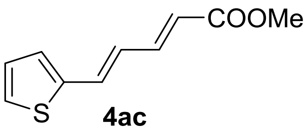
4aa

(2*E*,4*E*)-methyl 5-(naphthalen-1-yl)penta-2,4-dienoate (**4aa**). Yellow solid (156 mg from 2-(naphthalen-1-yl)ethanol **1aa** and methyl acrylate **2a**, isolated yield 65%). M.p. 48-49 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H),7.87 (d, *J* = 7.5 Hz, 1H),7.84 (d, *J* = 8.5 Hz, 1H),7.74-7.70 (m, 2H),7.61 (dd, *J* = 15.5 Hz, *J* = 11 Hz, 1H),7.57-7.52 (m, 2H),7.48 (t, *J* = 8 Hz, 1H),6.96 (dd, *J* = 15.5 Hz, *J* = 11 Hz, 1H),6.06 (d, *J* = 15 Hz, 1H),3.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 145.1, 137.4, 133.8, 133.3, 131.2, 129.6, 128.9, 128.9, 126.7, 126.2, 125.6, 124.3, 123.3, 121.2, 51.8.



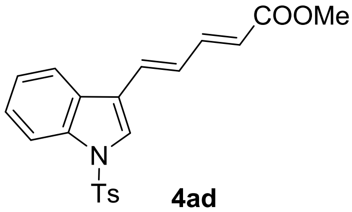
4ab

(2*E*,4*E*)-methyl 5-(benzo[b]thiophen-3-yl)penta-2,4-dienoate (**4ab**). Red liquid (235 mg from 2-(benzo[b]thiophen-3-yl)ethanol **1ab** and methyl acrylate **2a**, isolated yield 96%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8 Hz, 1H),7.88 (d, *J* = 8 Hz, 1H), 7.64 (s, 1H), 7.52 (dd, *J* = 15.5 Hz, *J* = 11.5 Hz, 1H), 7.47-7.44 (m, 1H),7.42-7.38 (m, 1H),7.19 (d, *J* = 15 Hz, 1H),6.96 (dd, *J* = 15.5 Hz, *J* = 11 Hz, 1H), 6.03 (d, *J* = 15 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 145.1, 140.6, 137.4, 133.2, 132.2, 127.4, 125.1, 124.9, 124.9, 123.2, 121.9, 120.9, 51.7.



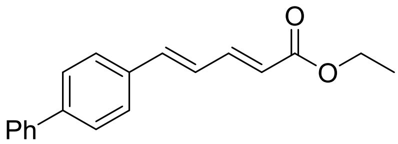
4ac

(2*E*,4*E*)-methyl 5-(thiophen-2-yl)penta-2,4-dienoate (**4ac**). Red solid (134 mg from 2-(thiophen-2-yl)ethanol **1ac** and methyl acrylate **2a**, isolated yield 69%). M.p. 82-84^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 15.5 Hz, *J* = 11 Hz, 1H), 7.29 (d, *J* = 5.5 Hz, 1H),7.11 (d, *J* = 3.5 Hz, 1H), 7.03-7.00 (m, 2H),6.67 (dd, *J* = 15 Hz, *J* = 11 Hz, 1H), 5.96 (d, *J* = 15 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 144.5, 141.5, 133.1, 128.6, 128.1, 126.9, 125.8, 120.5, 51.7.



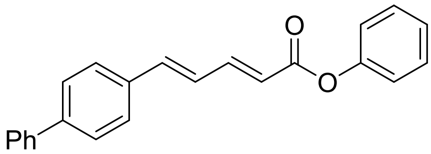
4ad

(2*E*,4*E*)-methyl 5-(1-tosyl-1H-indol-3-yl)penta-2,4-dienoate (**4ad**). Red solid (190 mg from 2-(1-tosyl-1H-indol-3-yl)ethanol **1ad** and methyl acrylate **2a**, isolated yield 50%). M.p. 124-126 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.79-7.75 (m, 4H),7.45 (dd, *J* = 15.5 Hz, *J* = 10 Hz, 1H),7.38-7.35 (m, 1H),7.32-7.29 (m, 1H),7.23 (d, *J* = 8 Hz, 2H), 6.98 (d, *J* = 15.5 Hz, 1H), 6.93 (dd, *J* = 16 Hz, *J* = 10 Hz, 1H),5.99 (d, *J* = 15 Hz, 1H), 3.78 (s, 3H),2.34 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 145.5, 145.2, 135.7, 135.0, 131.3, 130.2, 128.5, 127.1, 127.1, 126.0, 125.5, 124.0, 120.5, 120.4, 119.8, 114.0, 51.7, 21.7.



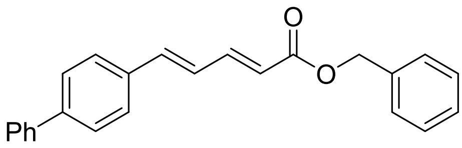
4ba

(2*E*,4*E*)-ethyl 5-([1,1'-biphenyl]-4-yl)penta-2,4-dienoate (**4ba**). Pale yellow solid (214 mg from 2-([1,1'-biphenyl]-4-yl)ethanol **1a** and ethyl acrylate **2b**, isolated yield 77%).M.p. 106-108 °C.The NMR data is identical to that reported in literature.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H),7.54 (d, *J* = 8.5 Hz,2H), 7.50-7.44 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H),6.96-6.89 (m, 2H),6.01 (d, *J* = 15.5 Hz, 1H),4.25 (q, *J* = 14.5 Hz, *J* = 7.5 Hz, 2H),1.33 (t, *J* = 7.5 Hz, 3H).



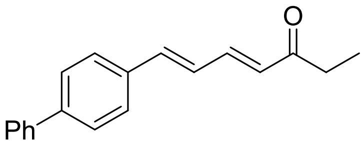
4ca

(2*E*,4*E*)-phenyl 5-([1,1'-biphenyl]-4-yl)penta-2,4-dienoate (**4ca**). Pale yellow solid(277 mg from 2-([1,1'-biphenyl]-4-yl)ethanol **1a** and phenyl acrylate **2c**, isolated yield 85%).M.p. 124-126 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 4H),7.58 (d, *J* = 8.5 Hz, 2H),7.46 (t, *J* = 7.5 Hz, 3H),7.42-7.38 (m, 3H), 7.24 (d, *J* = 7.5, 1H), 7.17-7.16 (m, 2H), 7.01 (d, *J* = 8.5 Hz, 2H),6.20 (d, *J* = 15 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 151.0, 146.7, 142.2, 141.2, 140.4, 135.0, 129.5, 129.0, 128.0, 127.9, 127.7, 127.1, 126.2, 125.8, 121.8, 120.3.



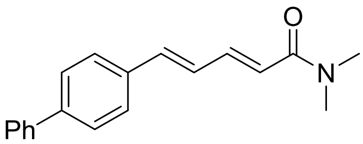
4da

(2*E*,4*E*)-benzyl 5-([1,1'-biphenyl]-4-yl)penta-2,4-dienoate (**4da**). White solid (296 mg from 2-([1,1'-biphenyl]-4-yl)ethanol **1a** and benzyl acrylate **2d**, isolated yield 87%).M.p. 124-125 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H),7.55-7.50 (m, 3H), 7.47-7.35 (m, 8H), 6.97-6.89 (m, 2H), 6.07 (d, *J* = 15.5 Hz, 1H),5.24 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 145.3, 142.0, 140.4, 140.4, 136.3, 135.1, 129.0, 128.7, 128.4, 128.3, 127.8, 127.8, 127.6, 127.1, 126.3, 121.0, 66.3.



4ea

(4*E*,6*E*)-7-([1,1'-biphenyl]-4-yl)hepta-4,6-dien-3-one (**4ea**). Pale yellow solid(231 mg from 2-([1,1'-biphenyl]-4-yl)ethanol **1a** and pent-1-en-3-one **2e**, isolated yield 88%).M.p. 112-114 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H),7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39-7.34 (m, 2H), 6.98 (d, *J* = 15.5 Hz, 1H), 6.92 (dd, *J* = 15.5 Hz, *J* = 10 Hz, 1H), 6.31 (d, *J* = 15.5 Hz, 1H), 2.64 (q, *J* = 7.5 Hz, 2H),1.16 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.2, 142.4, 142.0, 140.8, 140.4, 135.2, 129.5, 129.0, 127.8, 127.6, 127.1, 126.9, 34.1, 8.4.



4fa

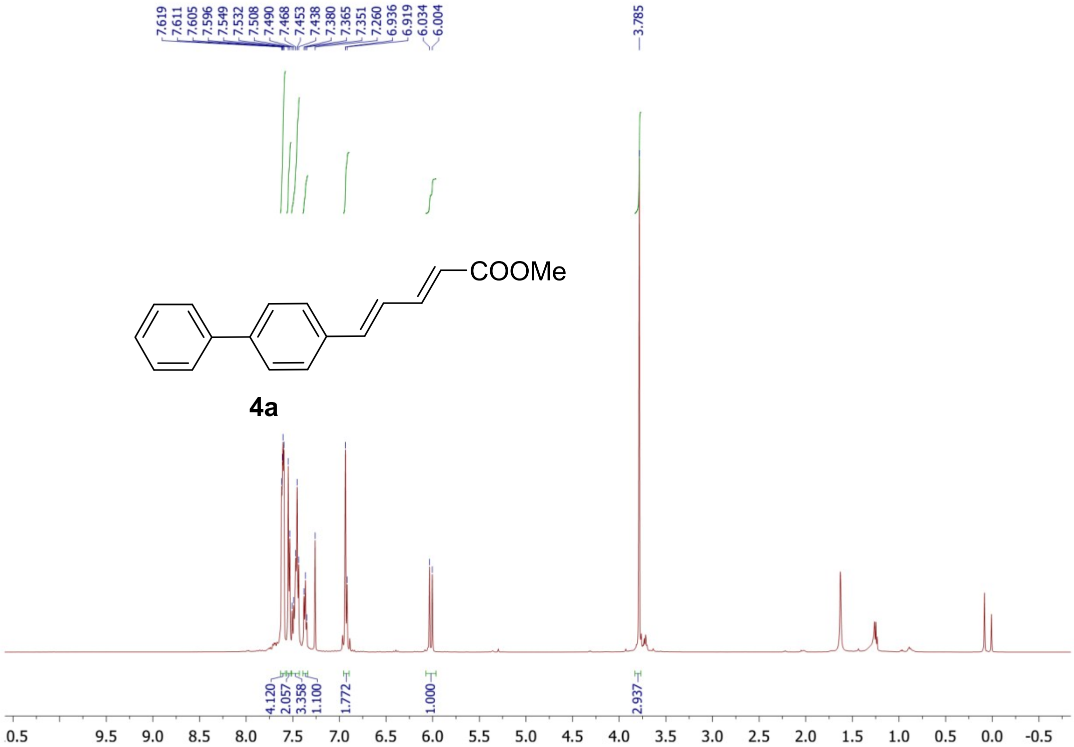
(2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)-N,N-dimethylpenta-2,4-dienamide (**4fa**). White solid (227 mg from 2-([1,1'-biphenyl]-4-yl)ethanol **1a** and N,N-dimethylacrylamide **2f**, isolated yield 82%).M.p. 146-148 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H),7.52 (d, *J* = 8.5 Hz, 2H), 7.50-7.43 (m, 3H), 7.35 (t, *J* = 7 Hz, 1H), 6.96 (dd, *J* = 15.5 Hz, *J* = 10 Hz, 1H),6.90 (d, *J* = 15.5 Hz, 1H), 6.48 (d, *J* = 14.5 Hz, 1H), 3.12 (s, 3H),3.05 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 142.6, 141.4, 140.5, 138.6, 135.6, 128.9, 127.7, 127.6, 127.5, 127.0, 120.8, 37.4, 36.0.

5. Reference

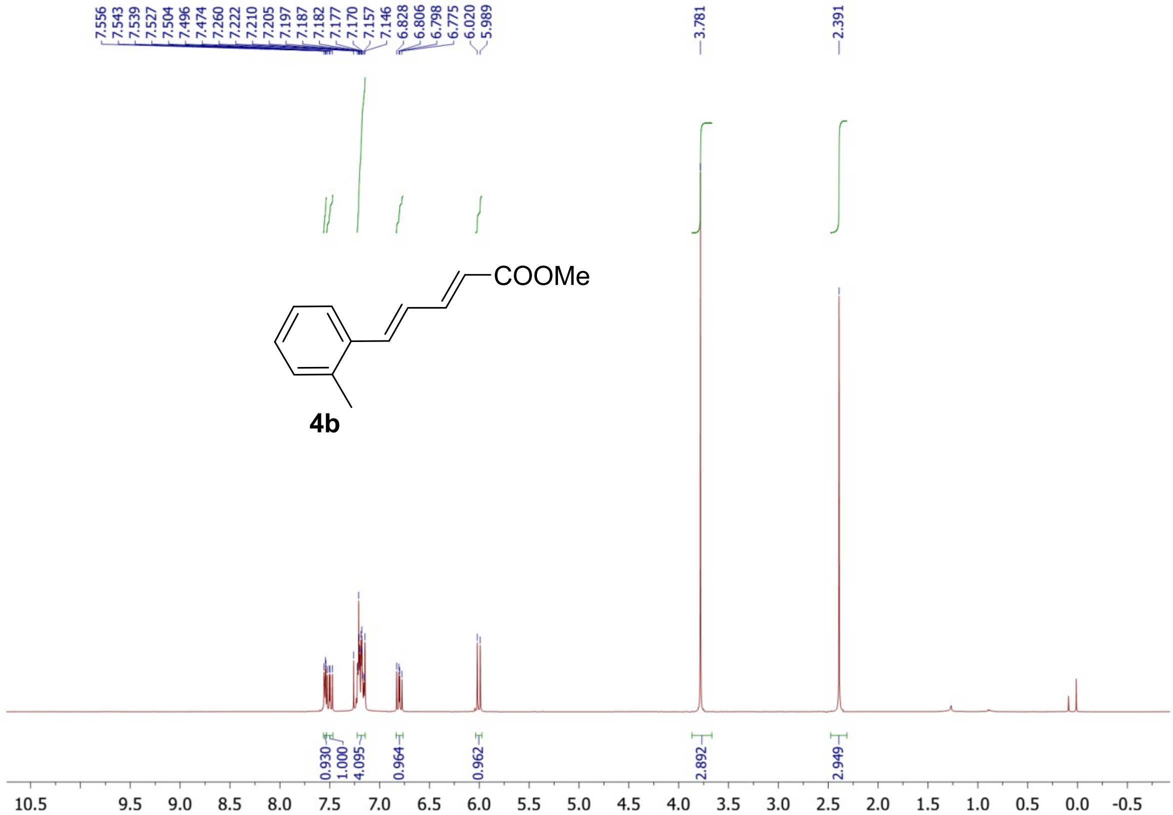
1. S. Ni, H. Wei, B. Li, F. Chen, Y. Liu, W. Chen, Y. Xu,X. Qiu, X. Li, Y. Lu, W. Liu, L. Hu, D. Lin, M. Wang,X. Zheng, F. Mao, J. Zhu, L. Lan and J. Li, *J. Med. Chem*.,2017, **60**, 8145.
2. T.Schabel and B.Plietker, *Chem. Eur. J*.,2013, **19**, 6938.
3. D. K. Barma, A. Kundu, A. Bandyopadhyay, A. Kundu,B.Sangras, A.Briot, C.Mioskowskib and J. R. Falck, *Tetrahedron Lett.,*2004, **45**, 5917.
4. A. Banerji et al., *J. Ind. Chem. Soc*.,2002, **79**, 876-883.
5. M. Harmata, K.Rayanil, V. R. Espejo andC. L. Barnes, *J. Org. Chem.,*2009, **74**, 3214.
6. S. Lang and R. J. K. Taylor,*Tetrahedron Lett.,*2006, **47**, 5489.
7. B. Li, S. Ni, F. Mao, F. Chen, Y. Liu, H. Wei, W. Chen,J. Zhu, L. Lan and J. Li, *J. Med. Chem*.,2018, **61**, 224.

6. NMR Spectra

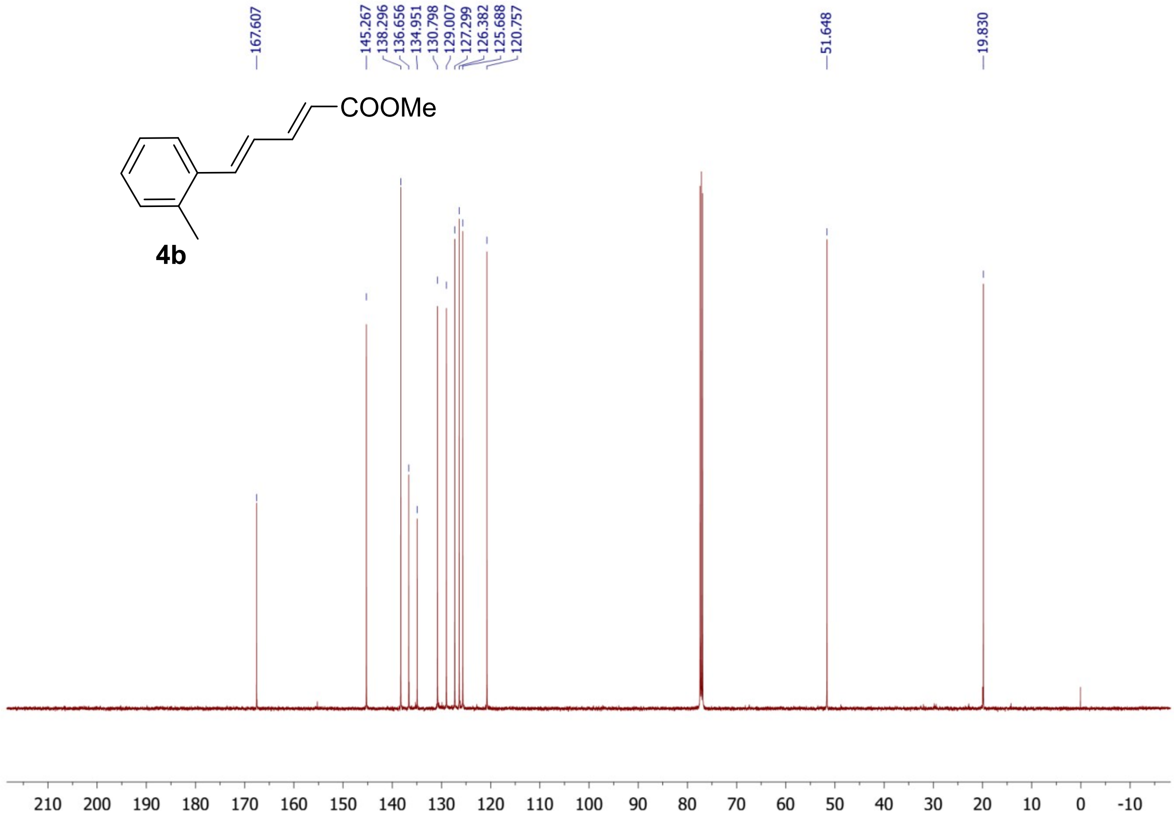
4a, -1H NMR, 500 MHz, $CDCl_3$



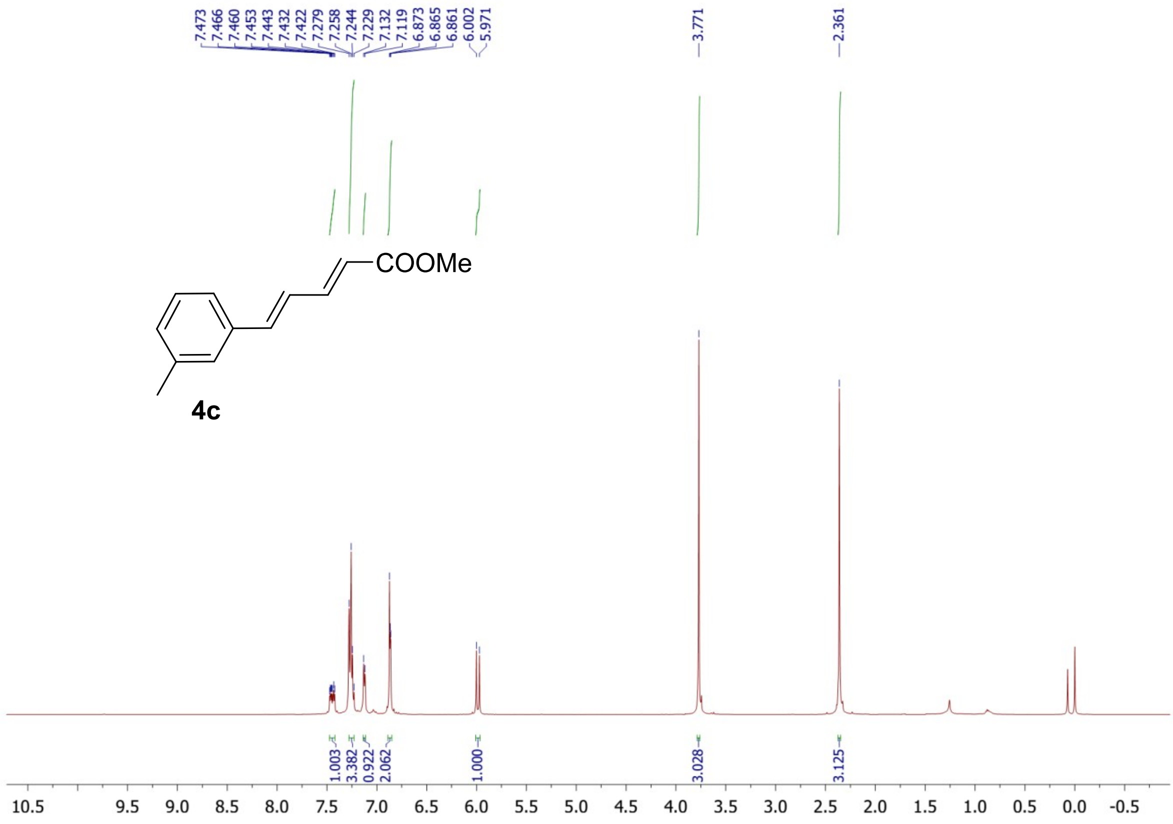
4b, -1H NMR, 500 MHz, $CDCl_3$



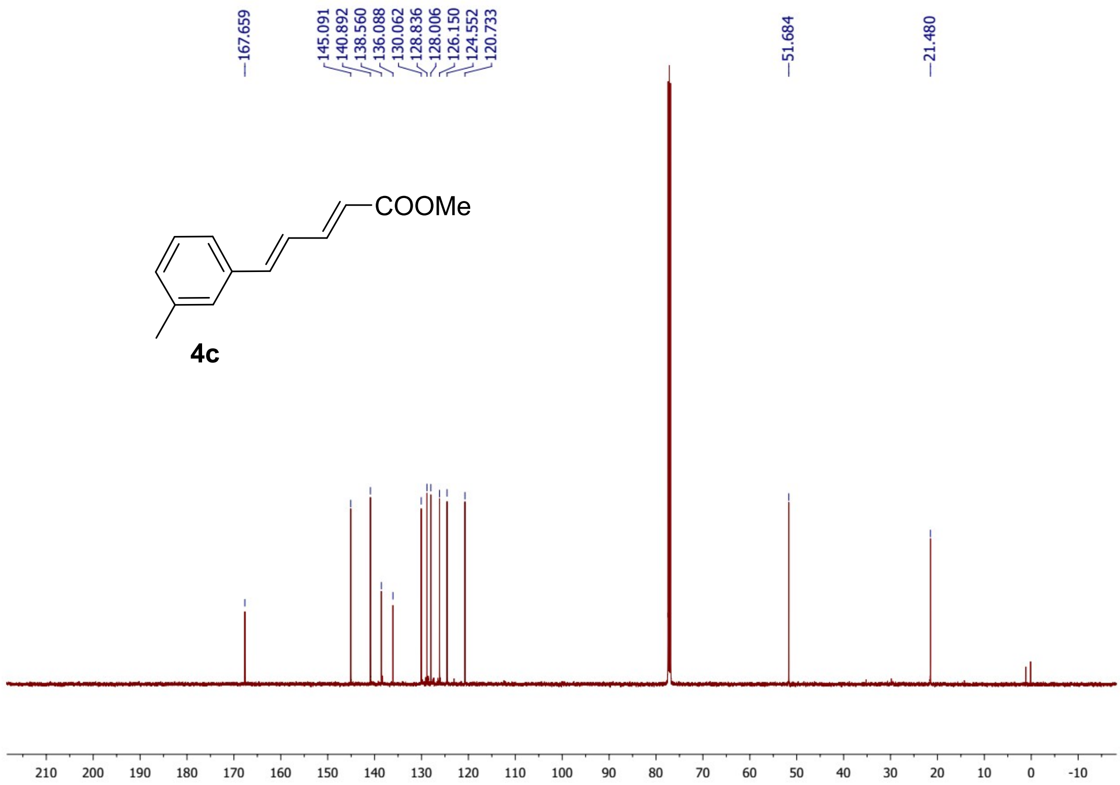
4b, -13C NMR, 126 MHz, $CDCl_3$



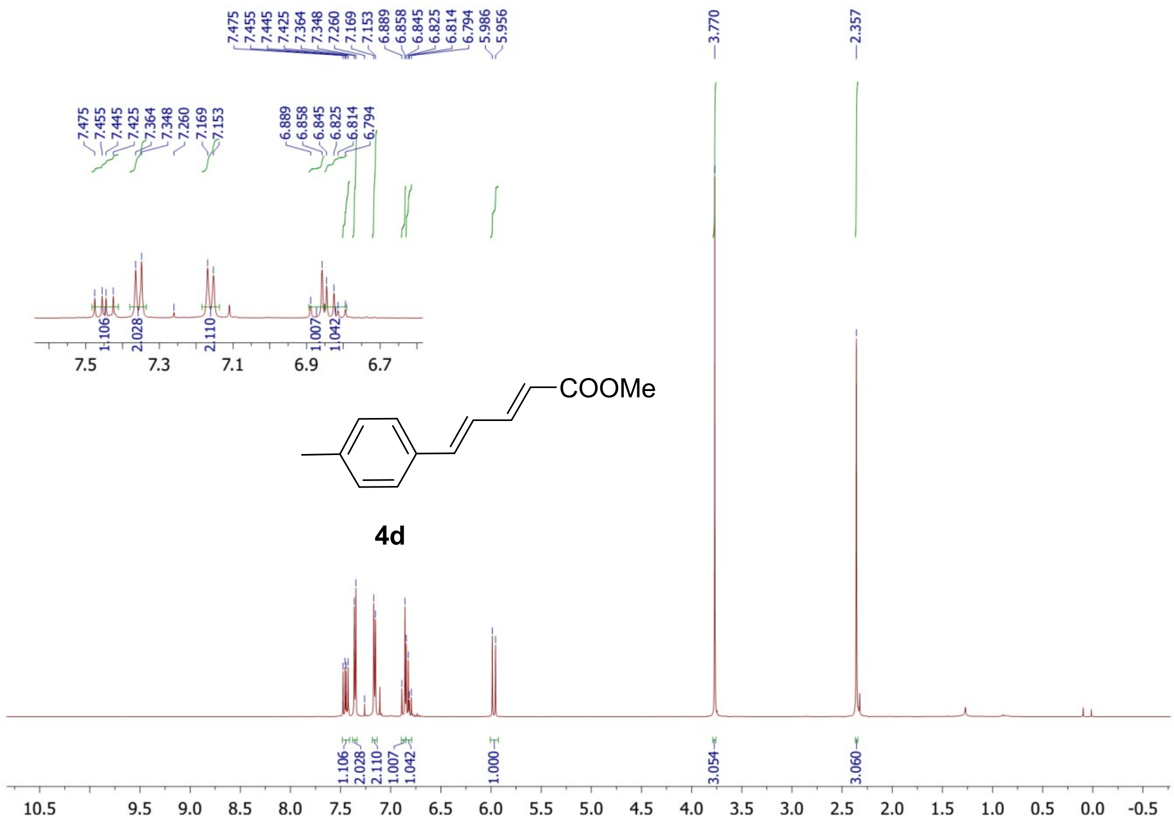
4c, -1H NMR, 500 MHz, $CDCl_3$



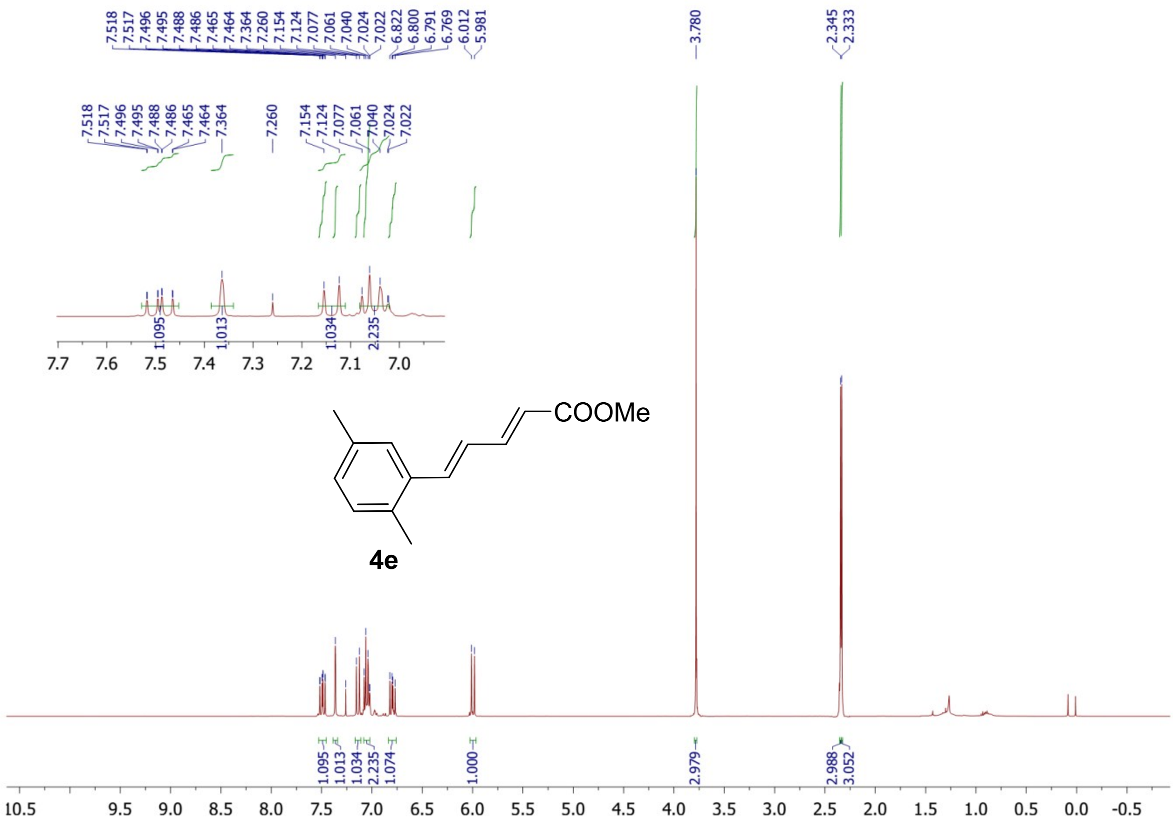
4c, -13C NMR, 126 MHz, $CDCl_3$



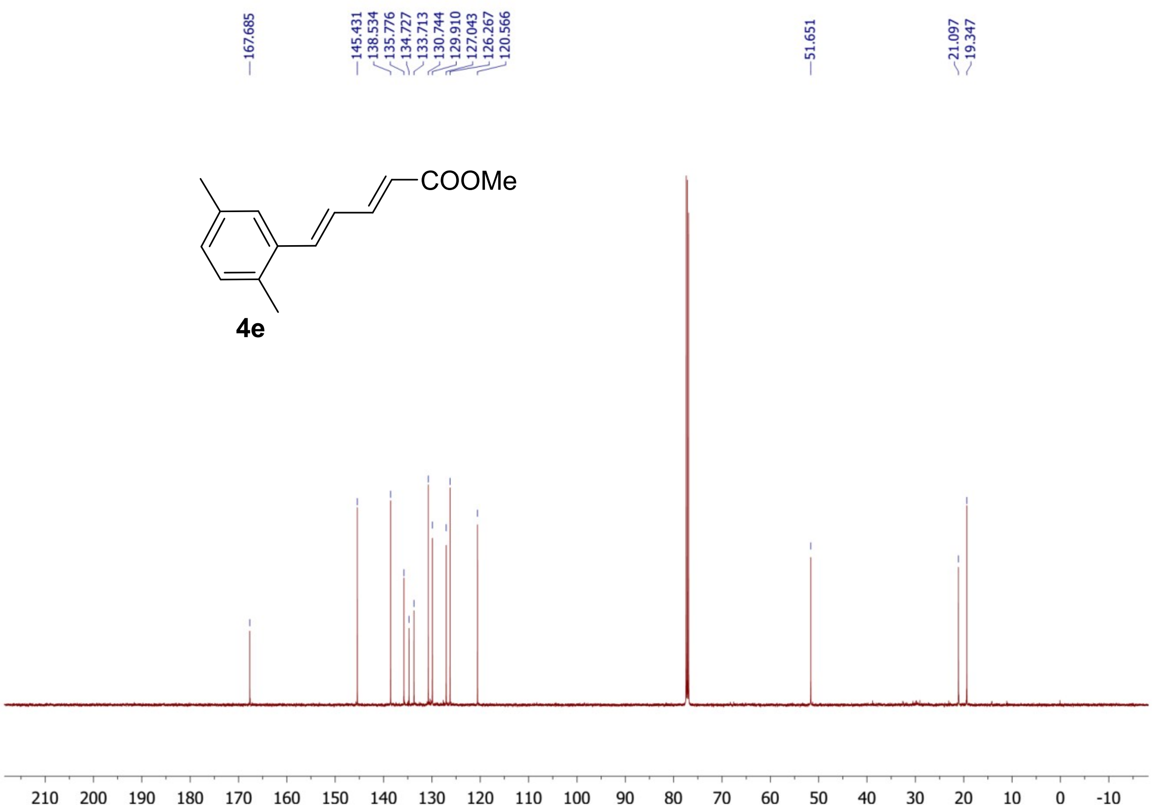
4d, -1H NMR, 500 MHz, $CDCl_3$



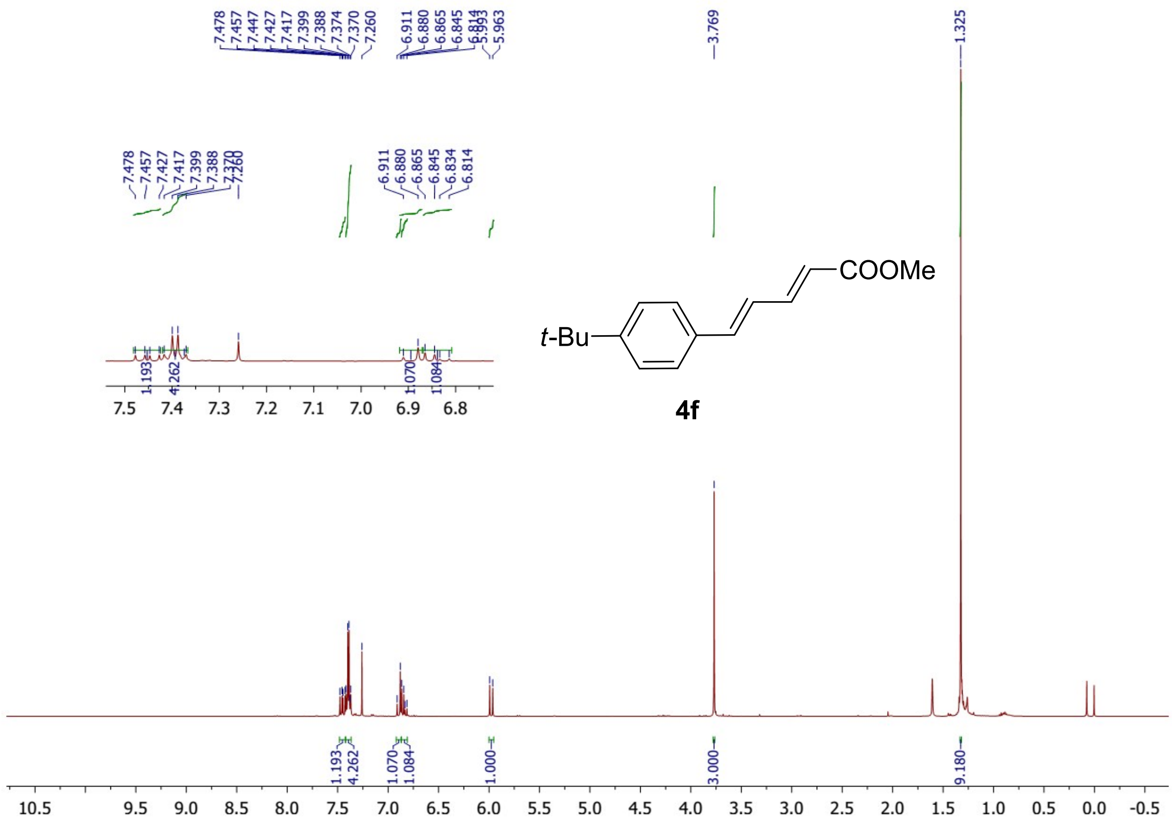
4e, -1H NMR, 500 MHz, $CDCl_3$



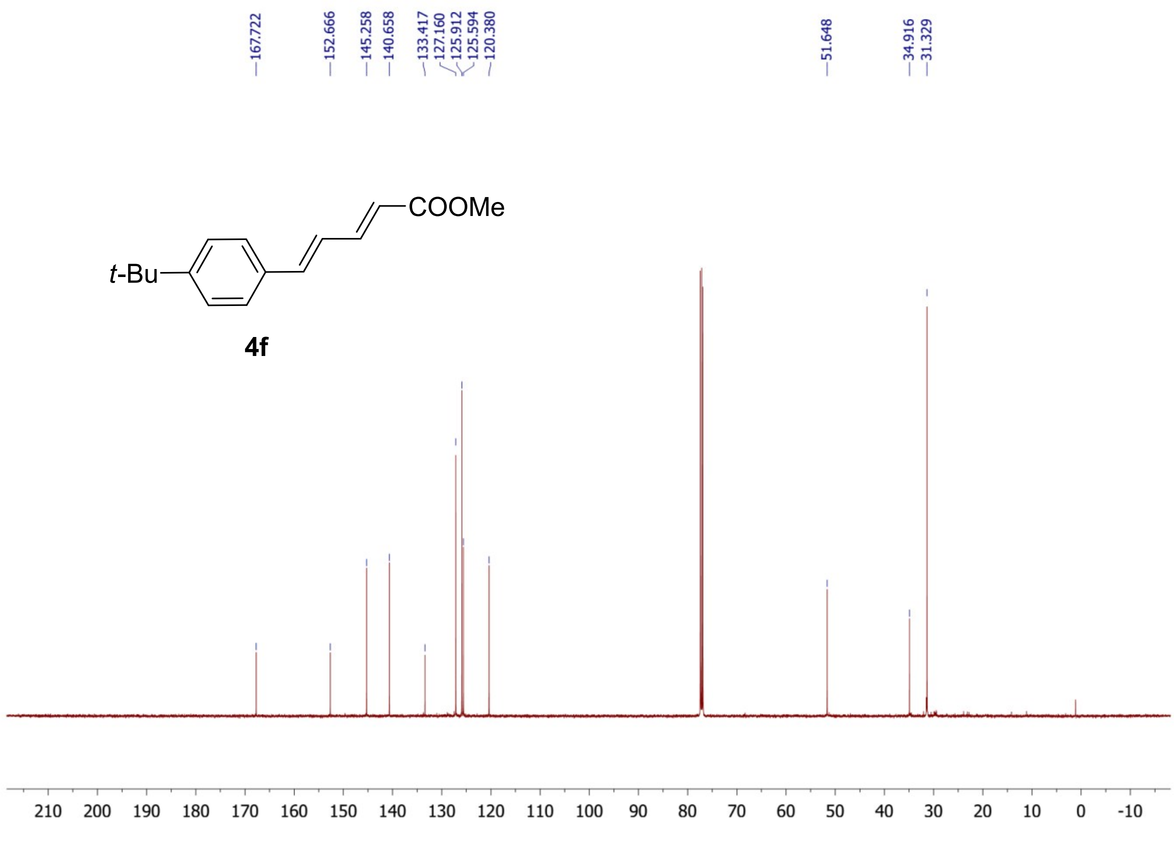
4e, -13C NMR, 126 MHz, $CDCl_3$



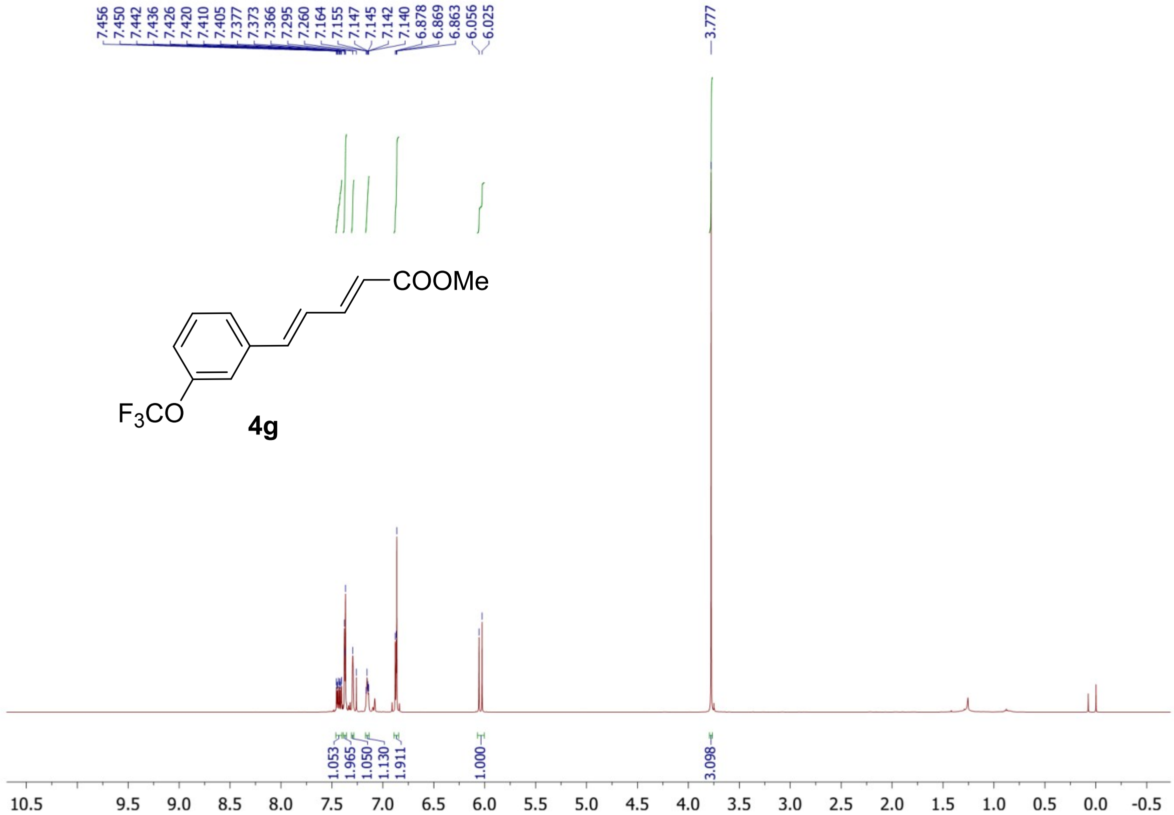
4f, -1H NMR, 500 MHz, $CDCl_3$



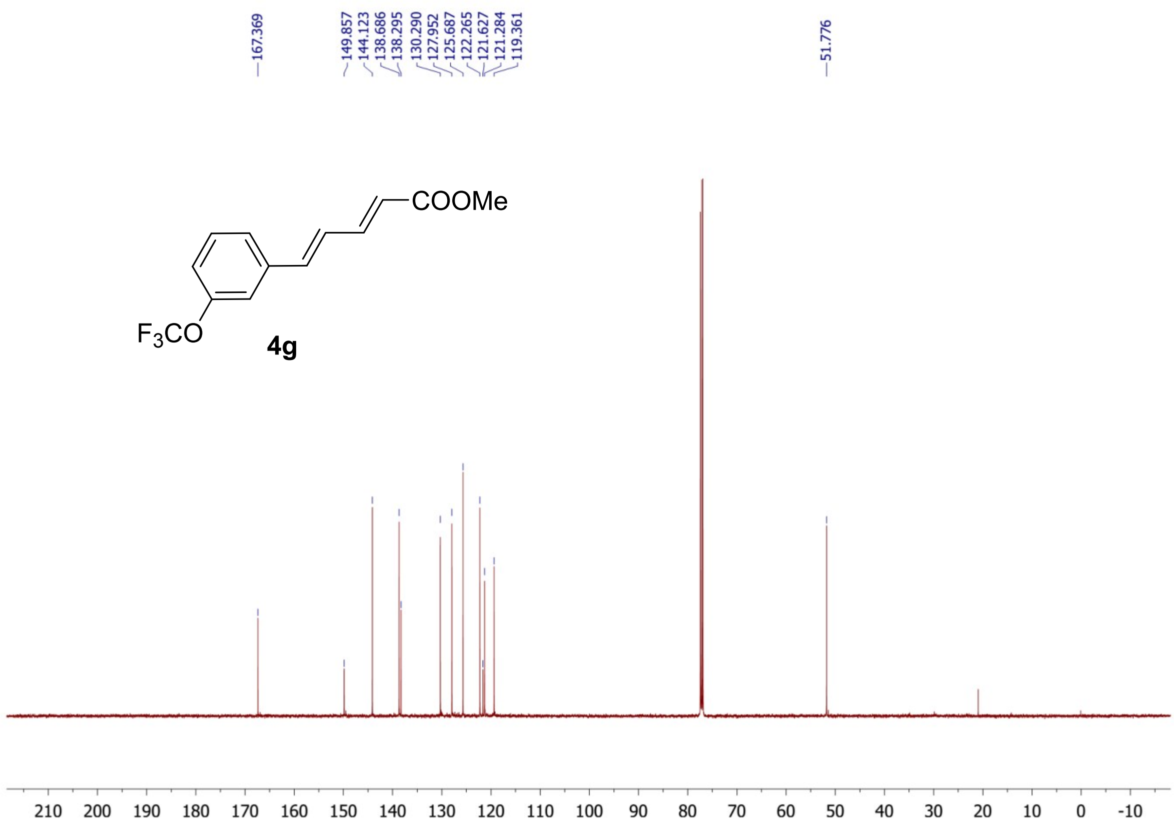
4f, -13C NMR, 126 MHz, $CDCl_3$



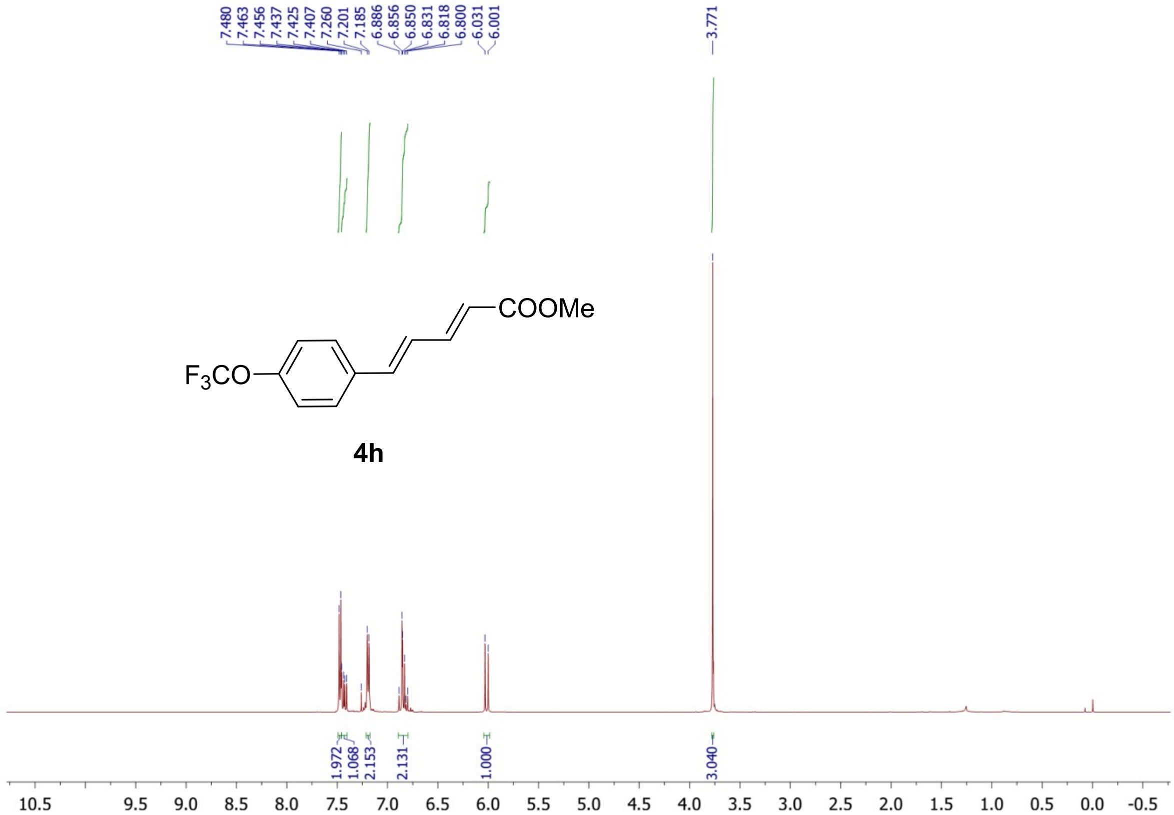
4g, -1H NMR, 500 MHz, $CDCl_3$



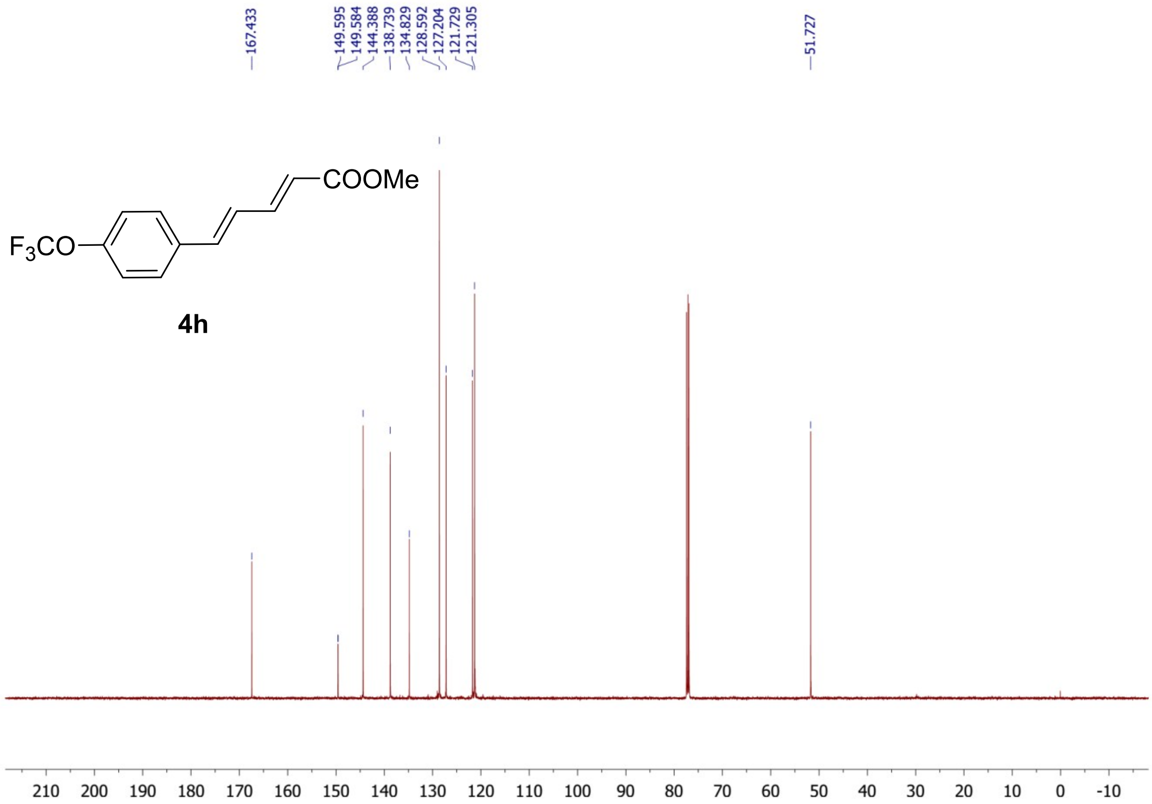
4g, -13C NMR, 126 MHz, $CDCl_3$



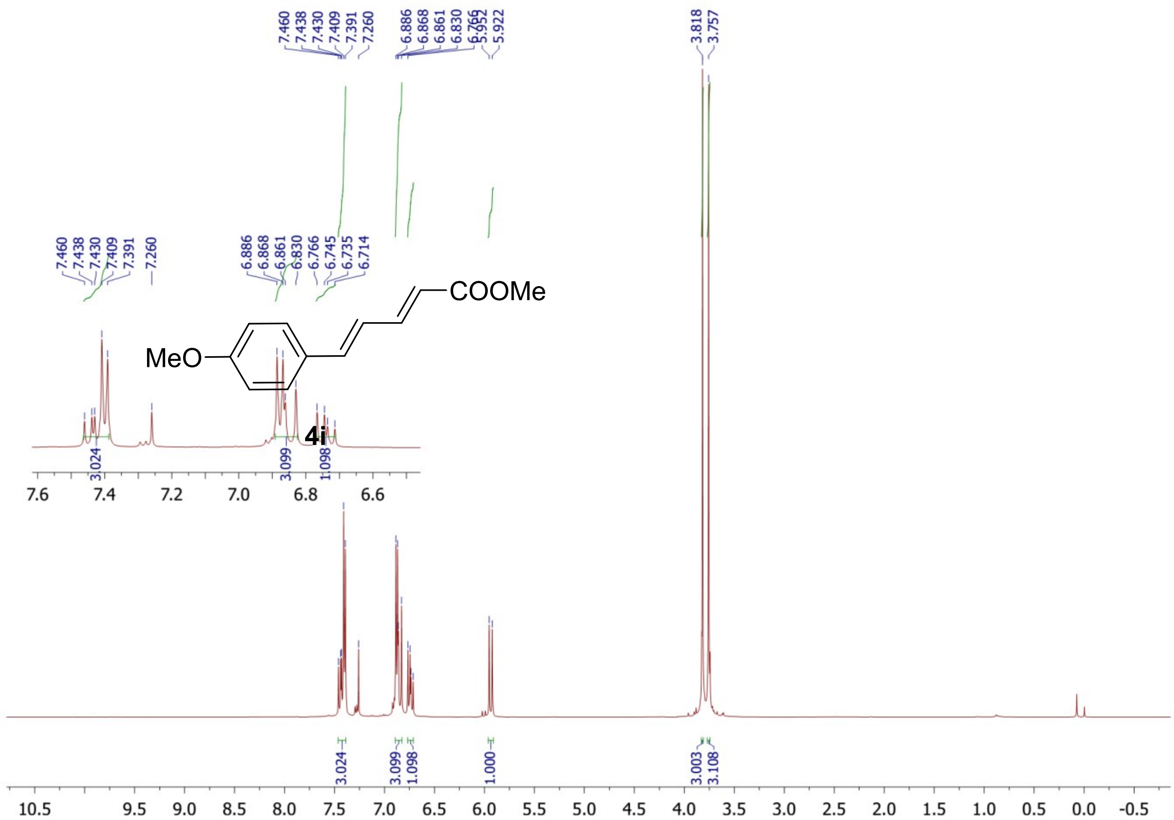
4h, -1H NMR, 500 MHz, $CDCl_3$



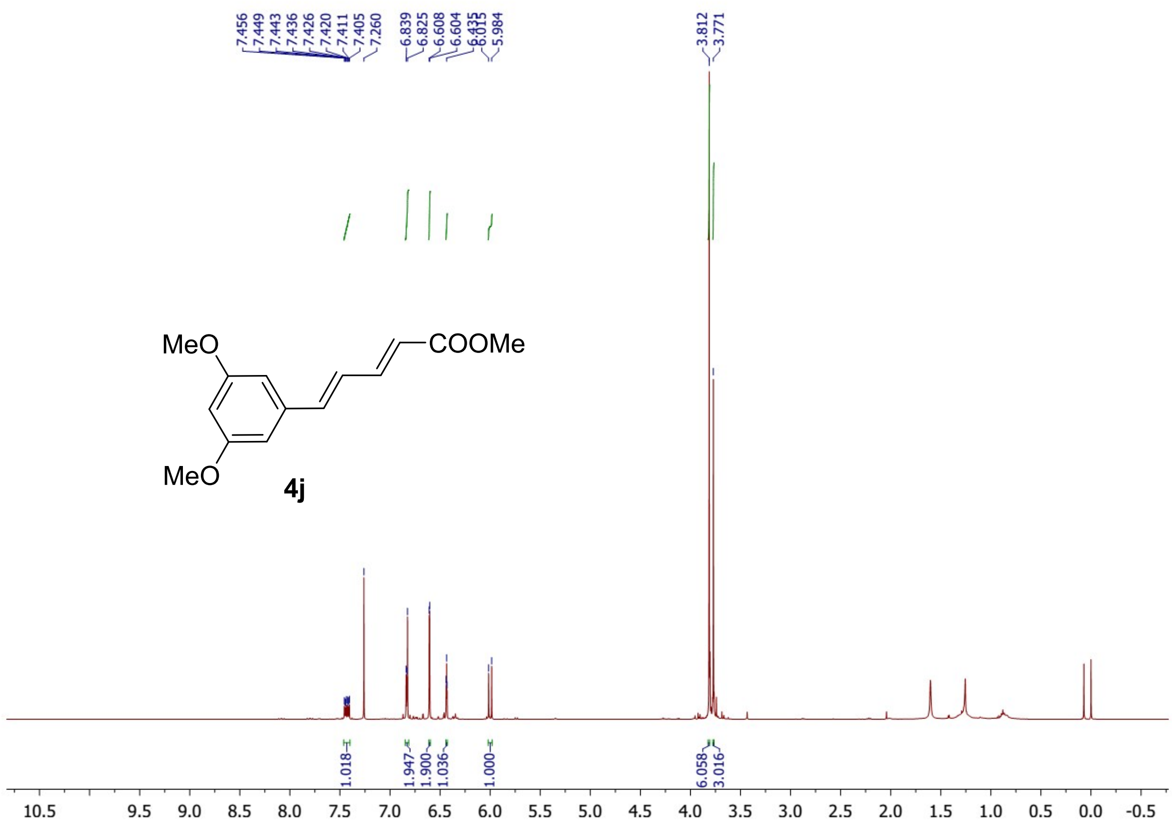
4h, -13C NMR, 126 MHz, $CDCl_3$



4i, -1H NMR, 500 MHz, $CDCl_3$



4j, -1H NMR, 500 MHz, $CDCl_3$



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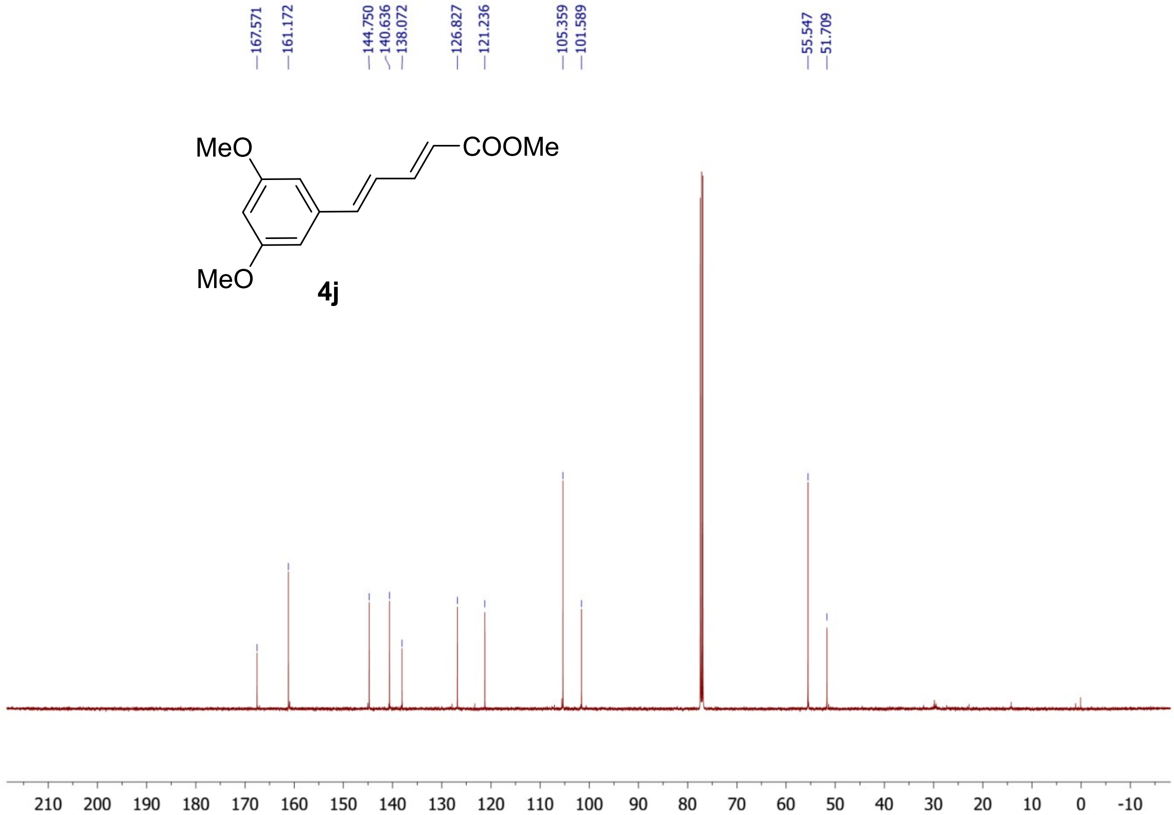
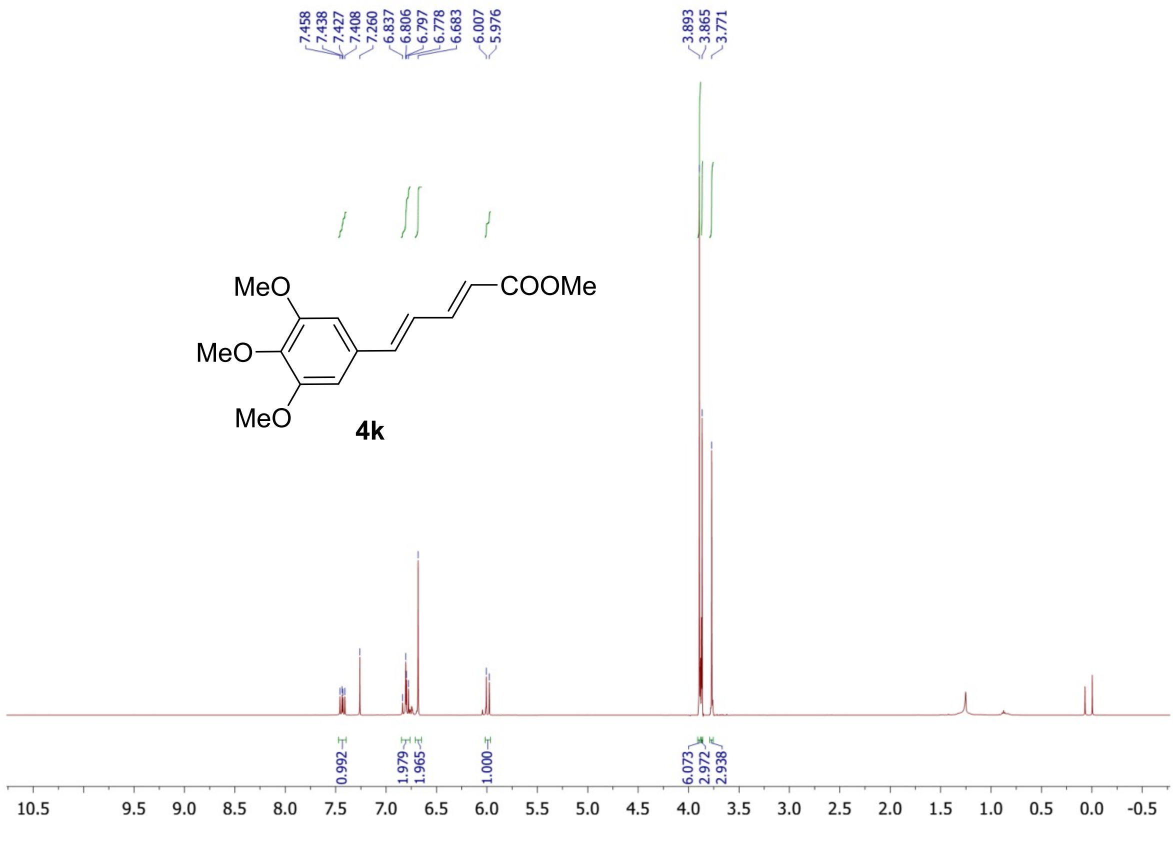
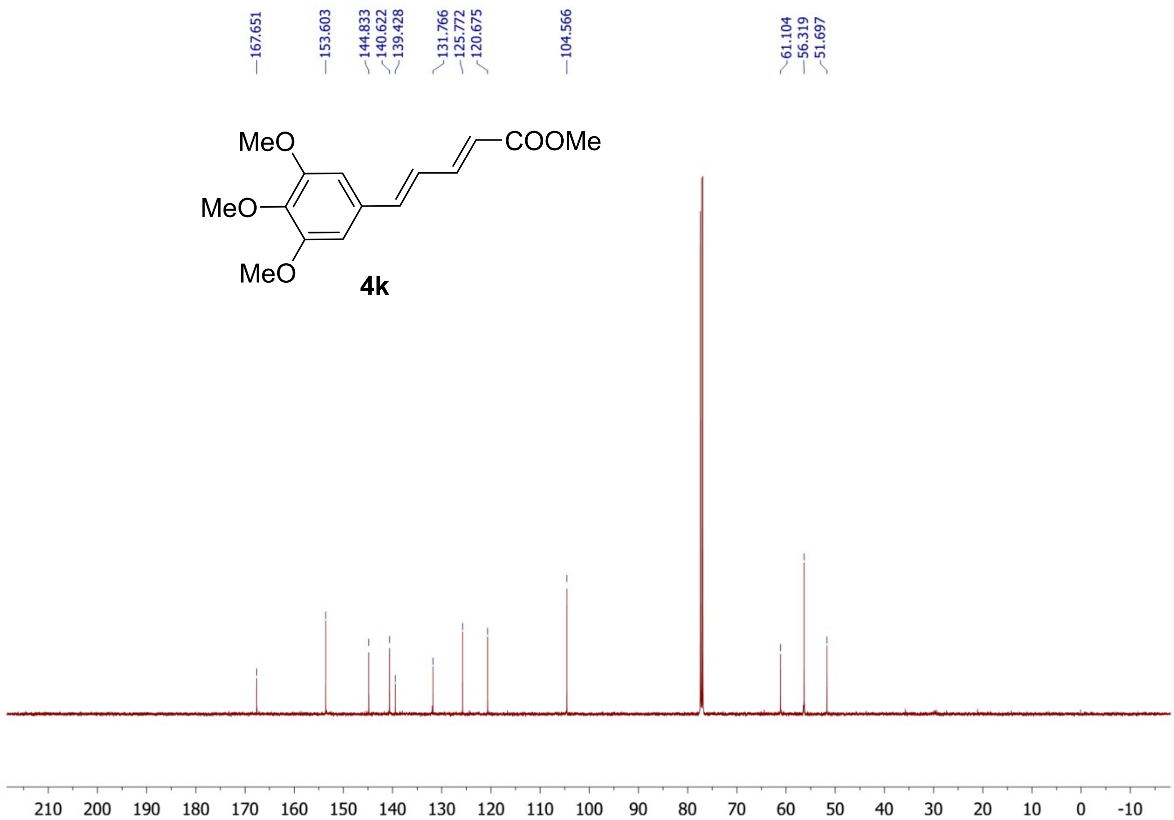


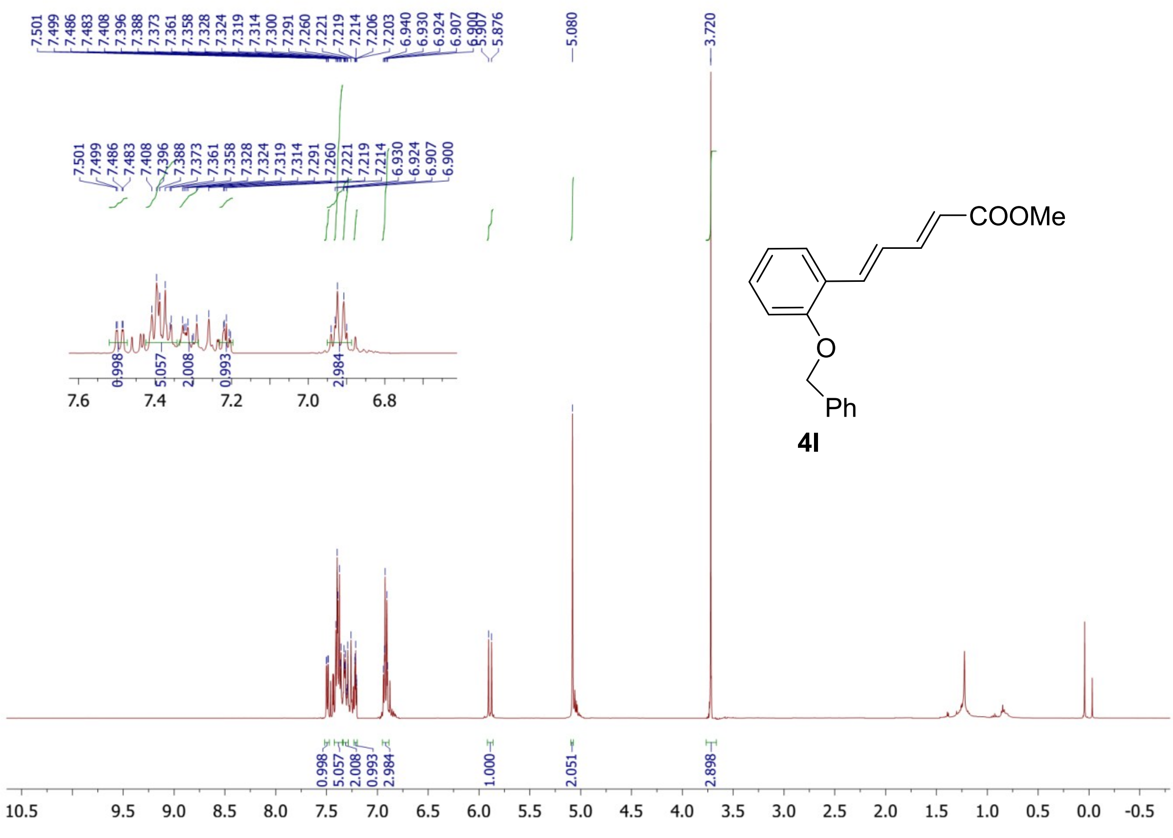
4k, -1H NMR, 500 MHz, $CDCl_3$



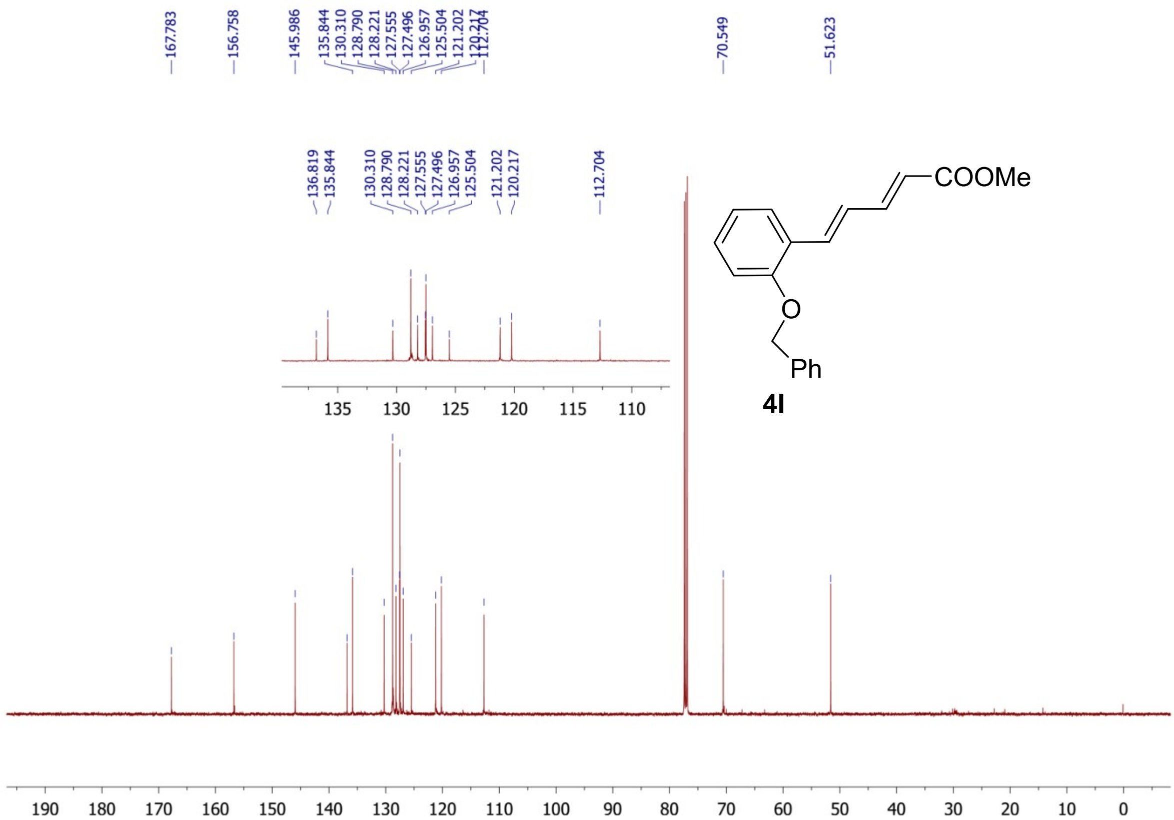
4k, -13C NMR, 126 MHz, $CDCl_3$



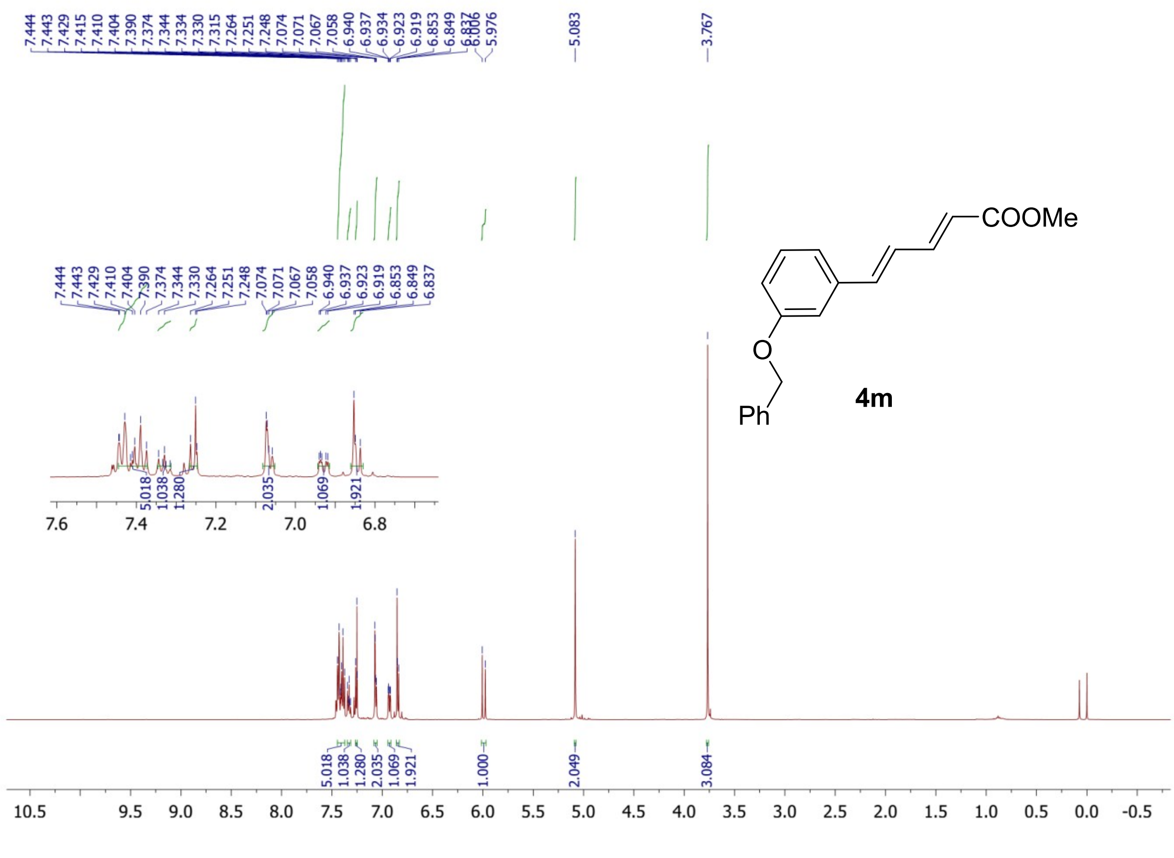
4l, -1H NMR, 500 MHz, $CDCl_3$



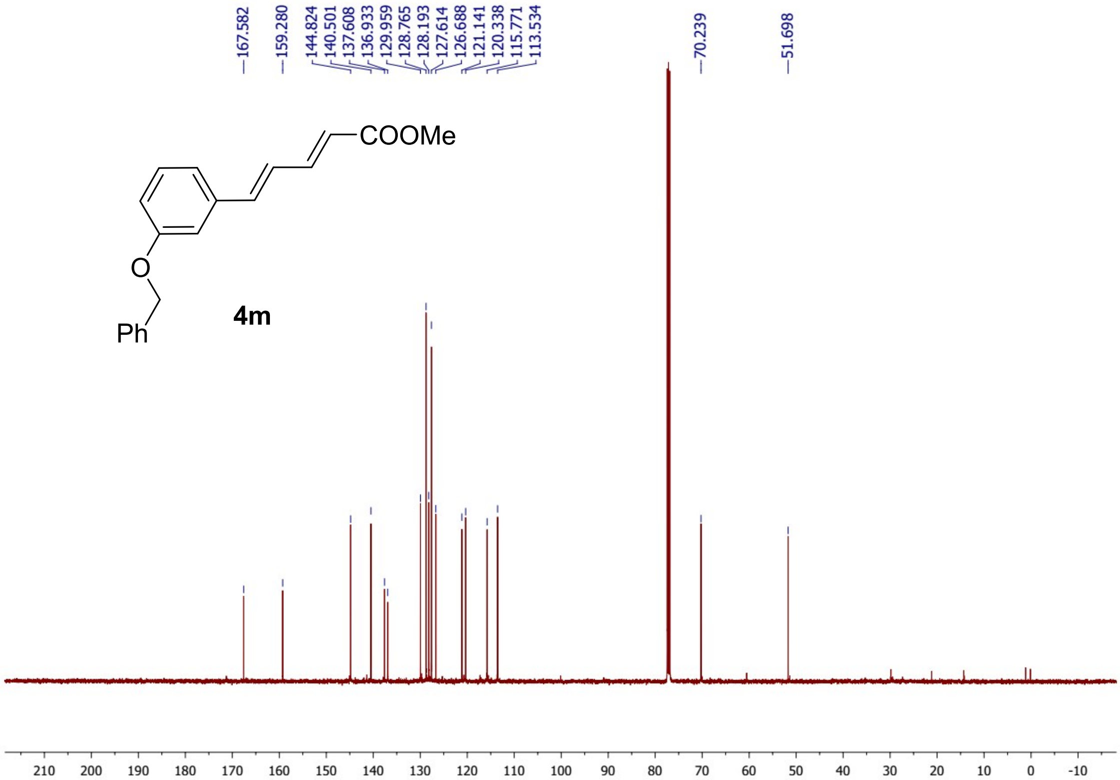
4l, -13C NMR, 126 MHz, $CDCl_3$



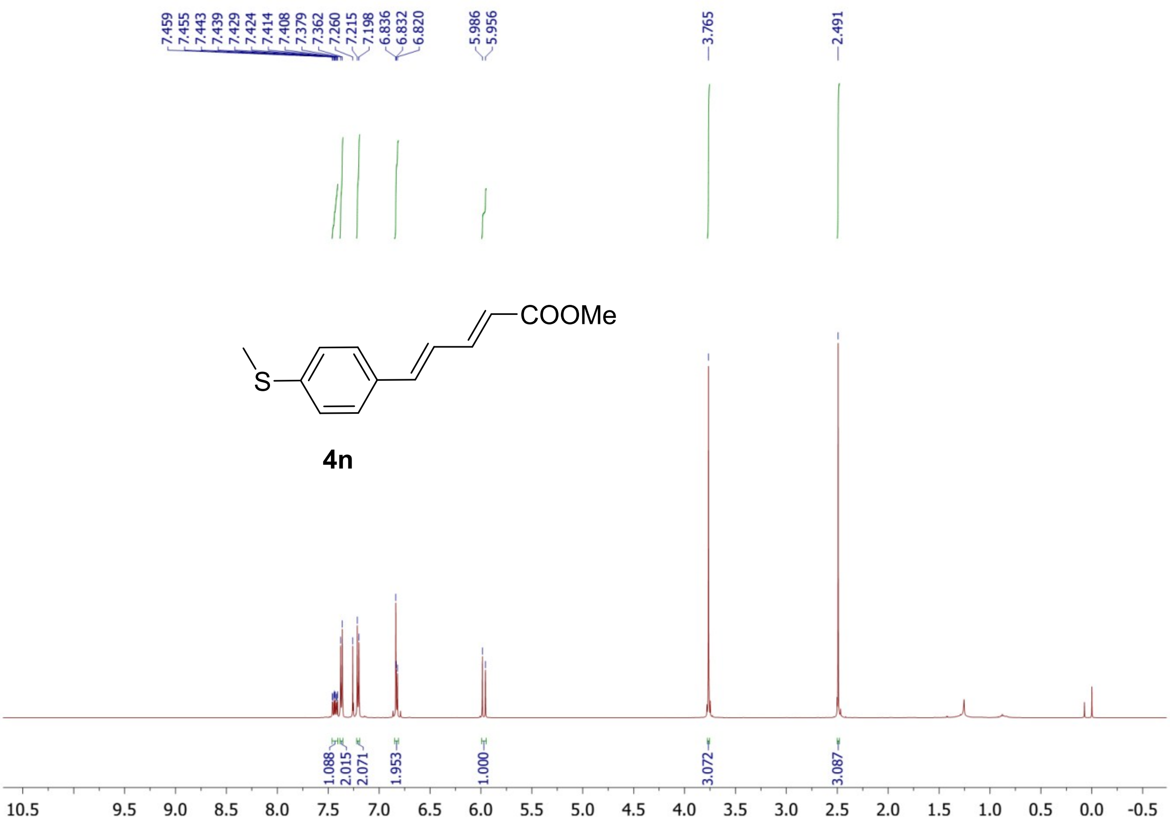
4m, -1H NMR, 500 MHz, $CDCl_3$



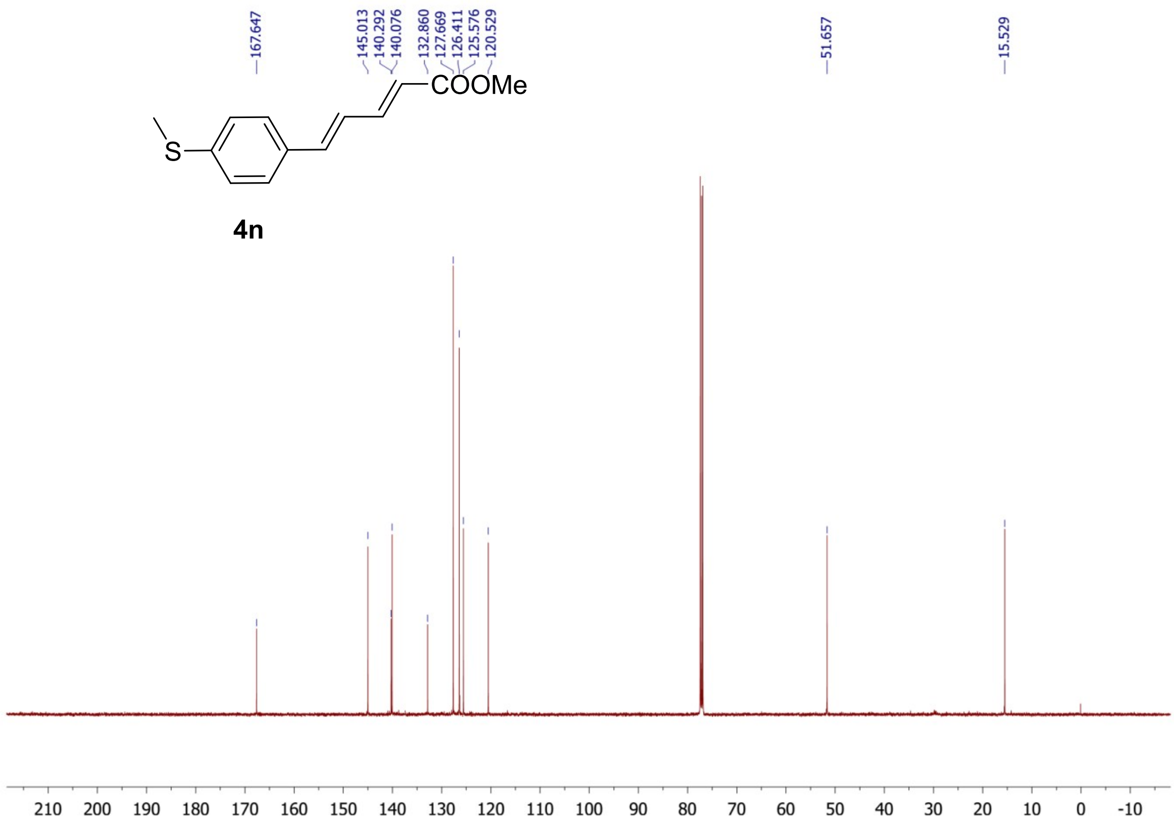
4m, -13C NMR, 126 MHz, $CDCl_3$



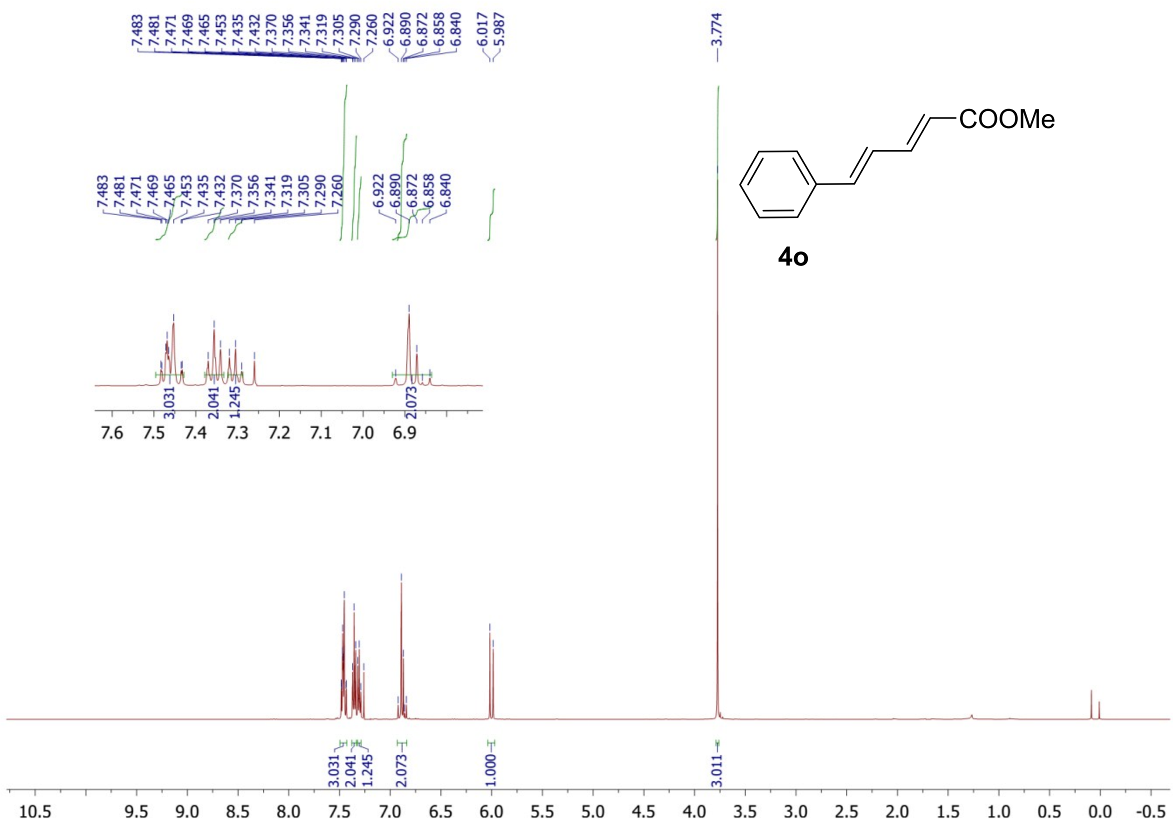
4n, -1H NMR, 500 MHz, $CDCl_3$



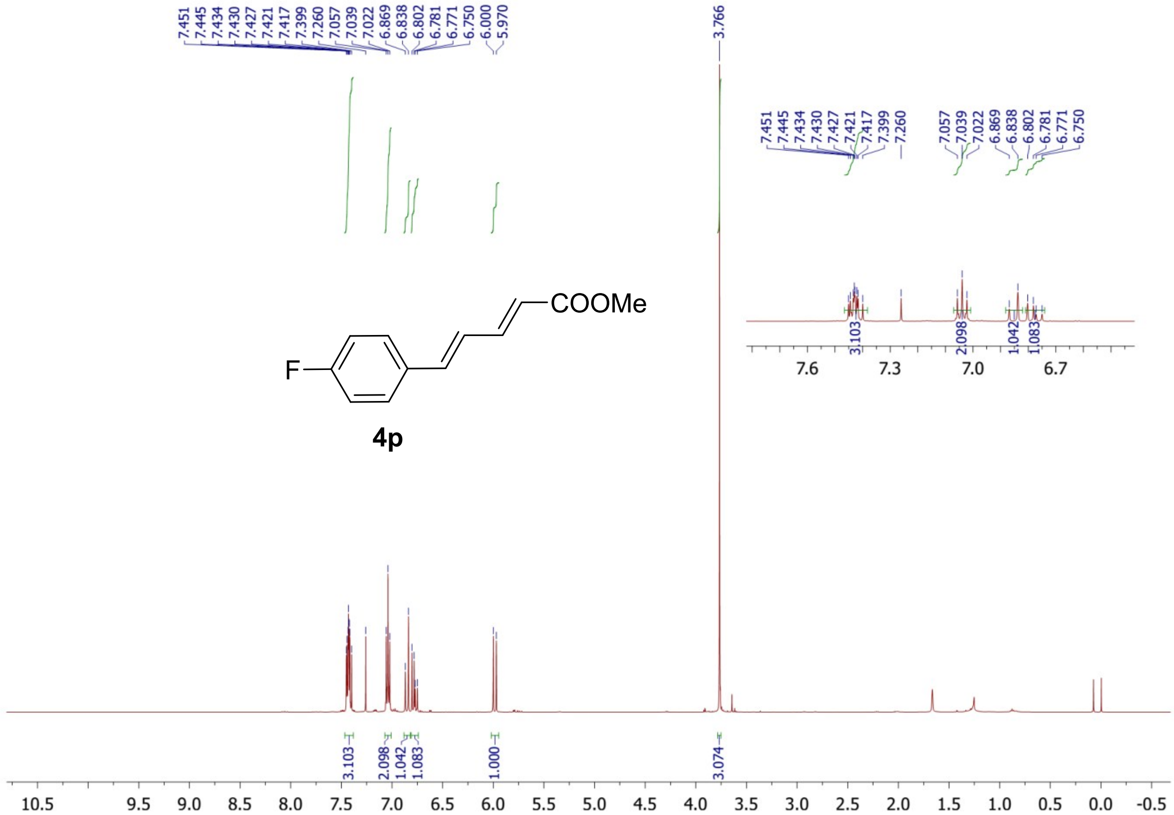
4n, -13C NMR, 126 MHz, $CDCl_3$



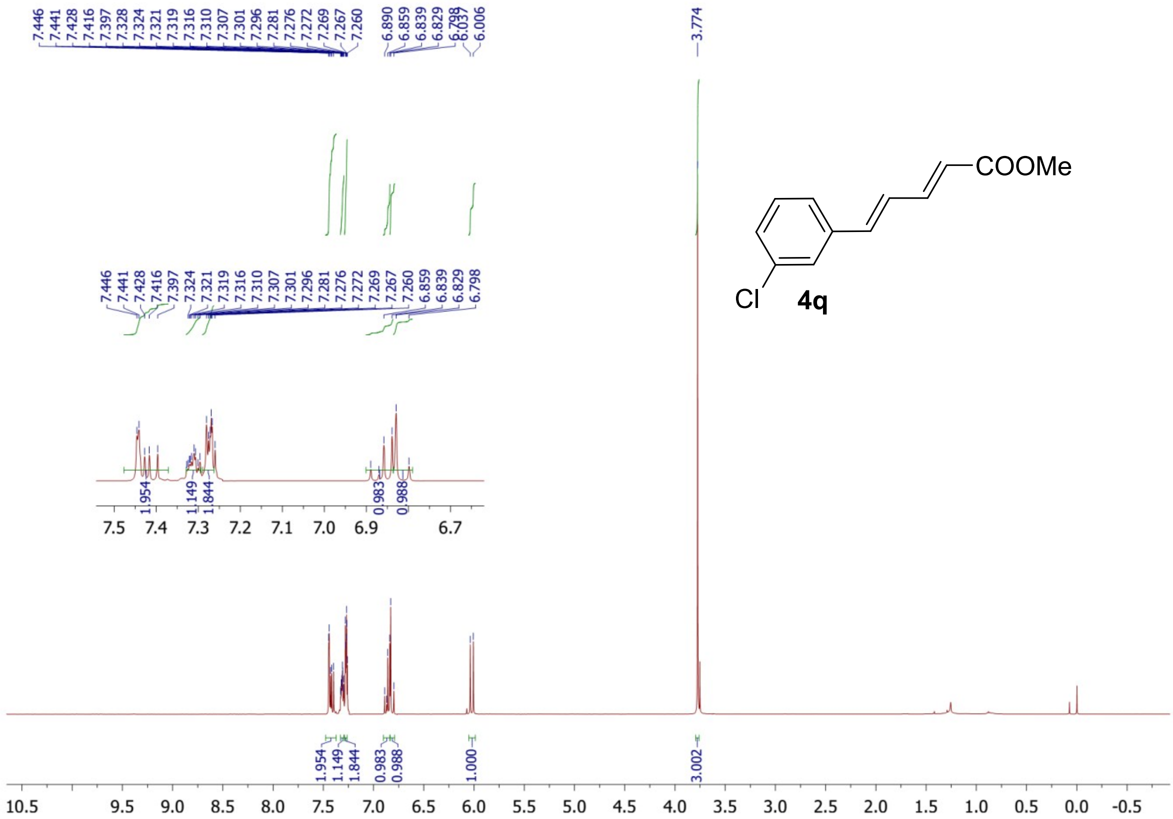
4o, -1H NMR, 500 MHz, $CDCl_3$



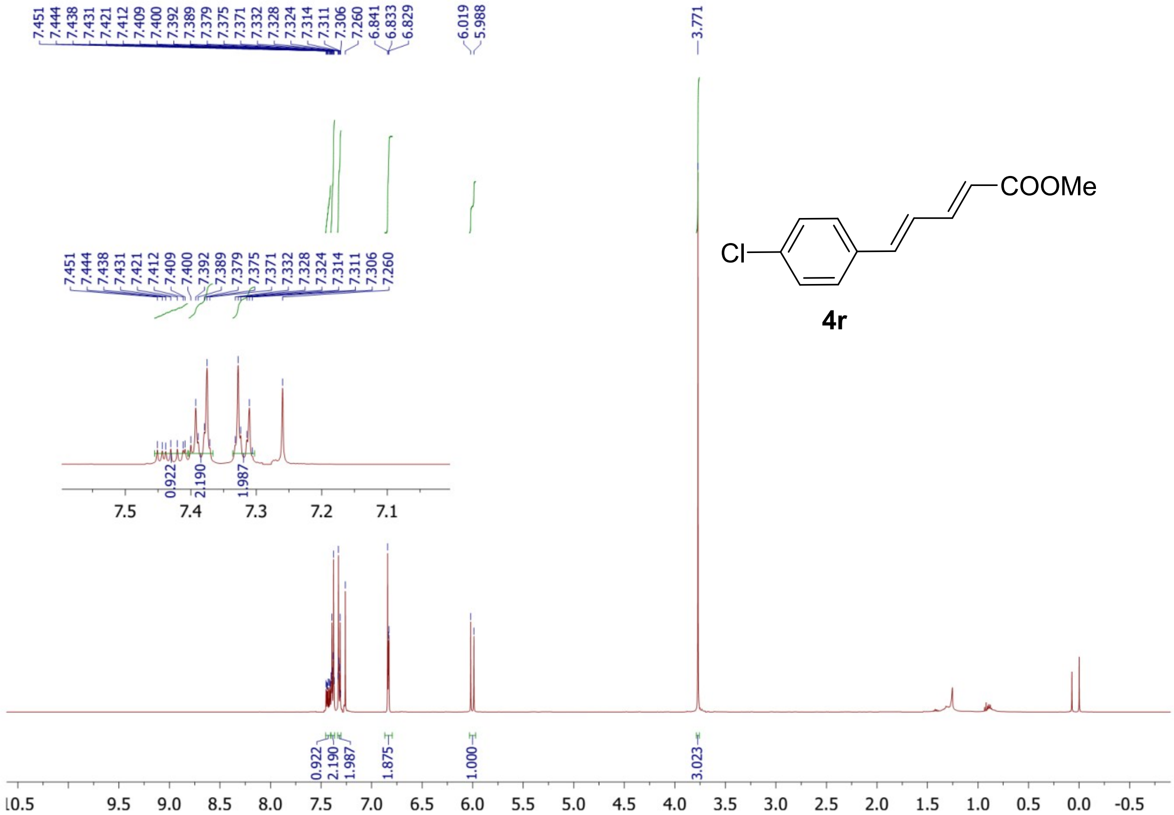
4p, -1H NMR, 500 MHz, $CDCl_3$



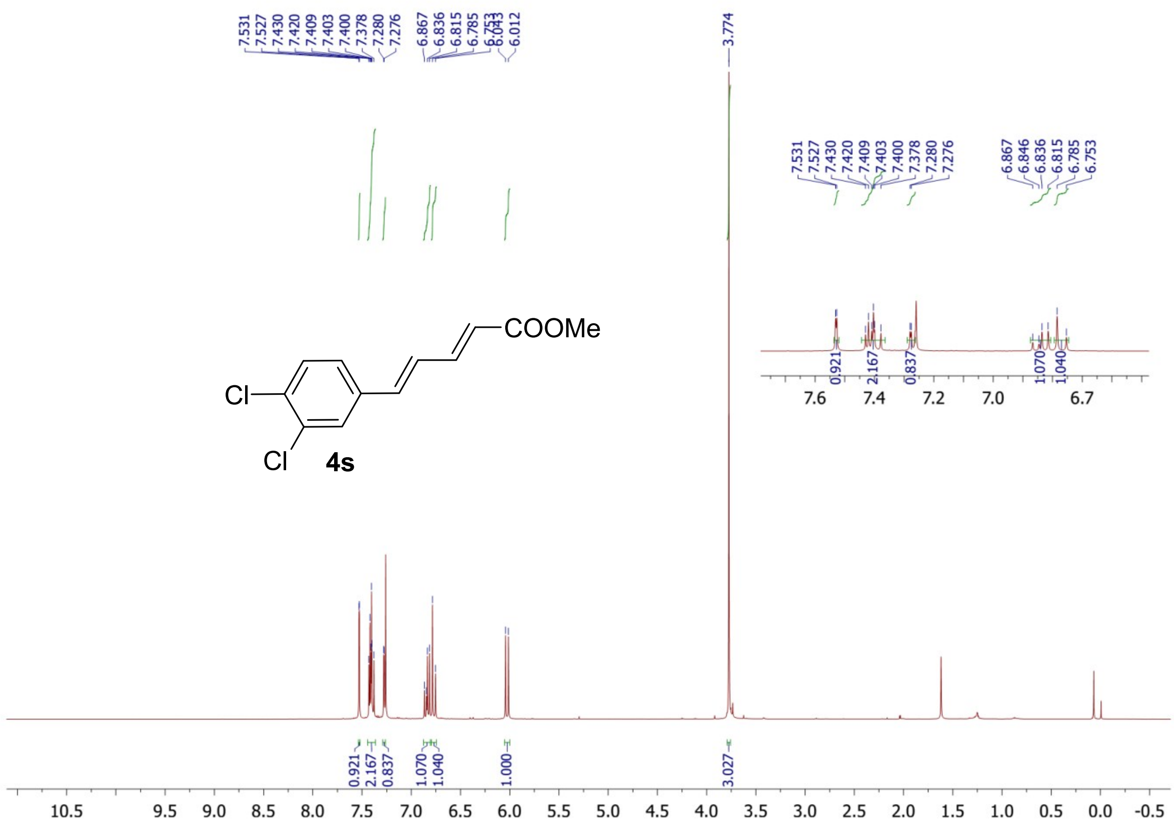
4q, -1H NMR, 500 MHz, $CDCl_3$



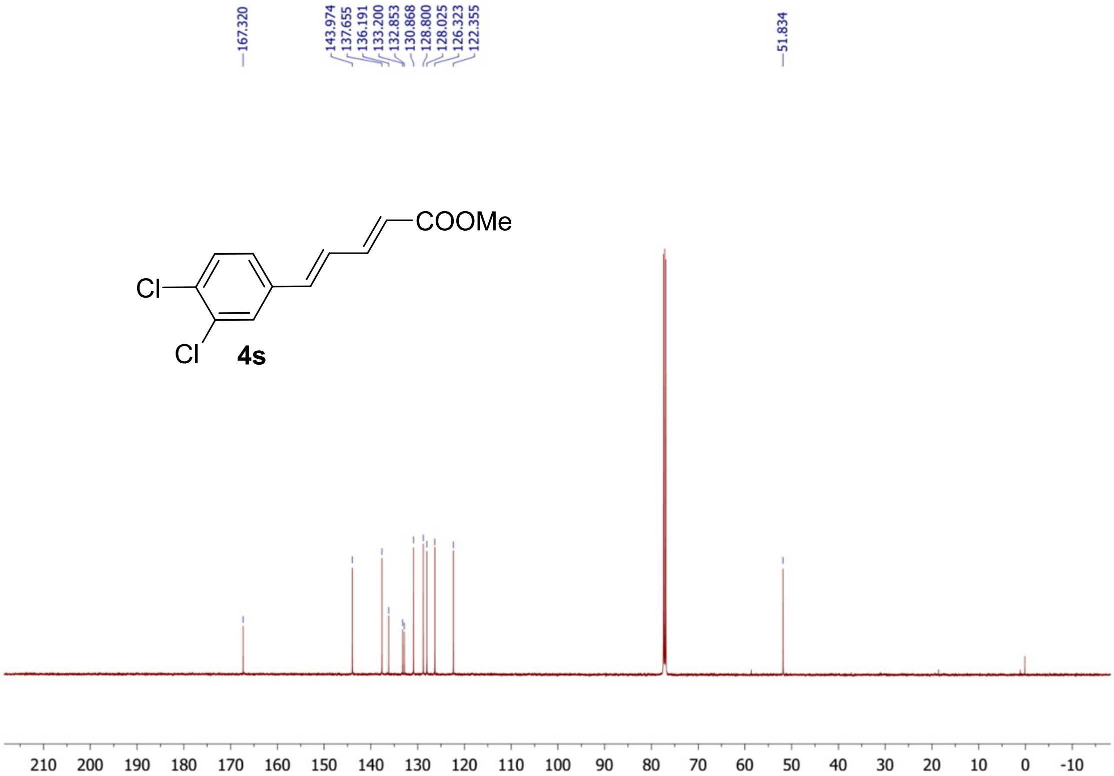
4r, -1H NMR, 500 MHz, $CDCl_3$



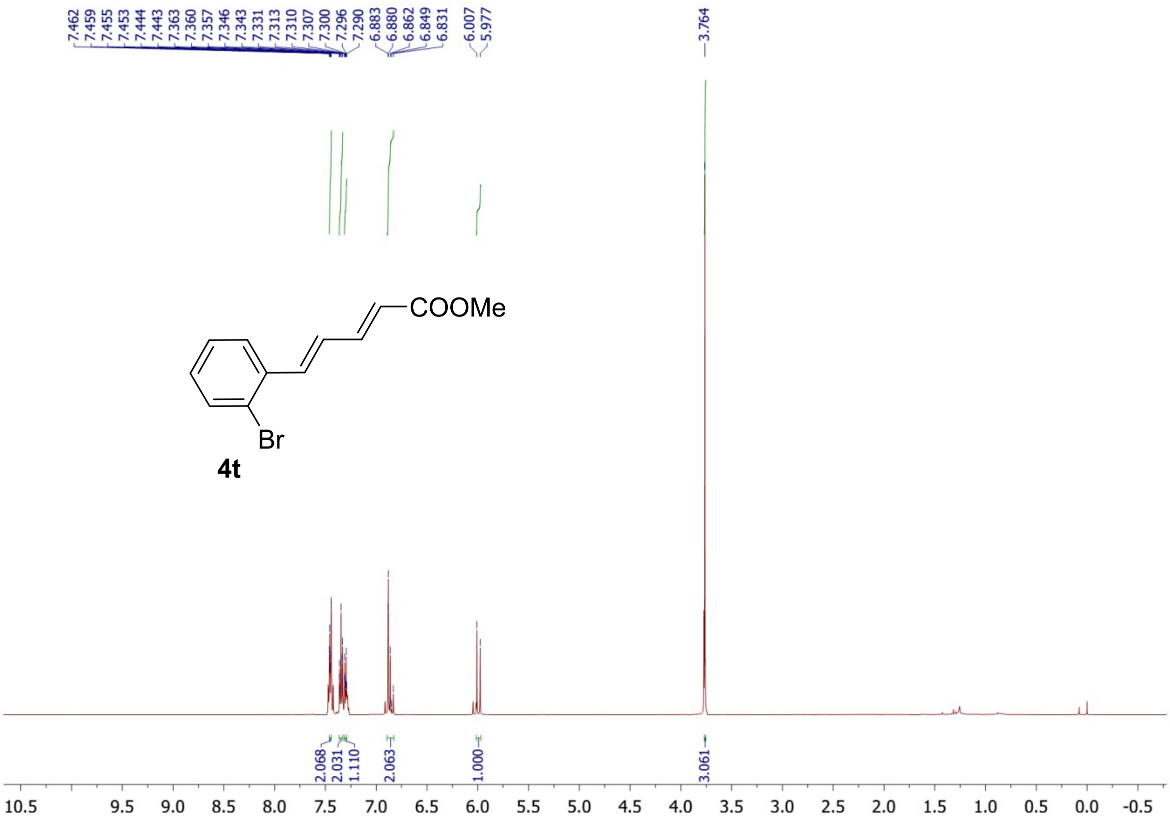
4s, -1H NMR, 500 MHz, $CDCl_3$



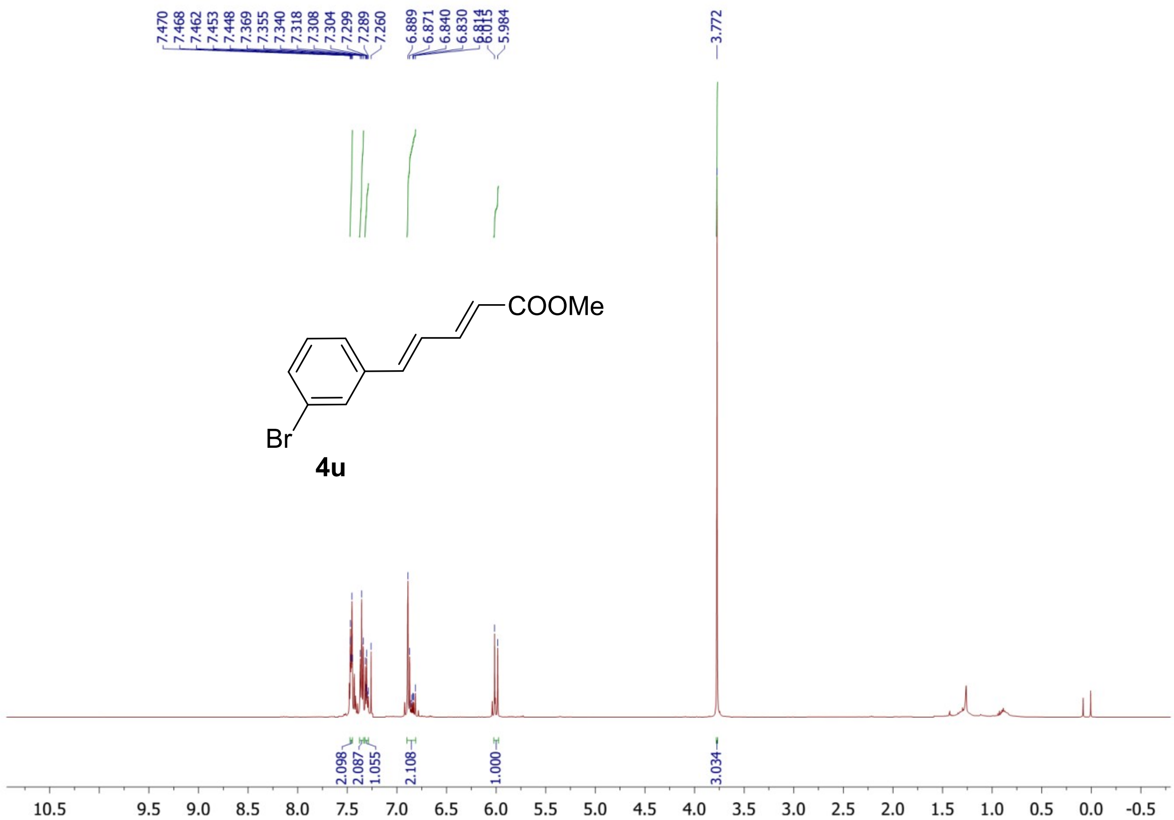
4s, -13C NMR, 126 MHz, $CDCl_3$



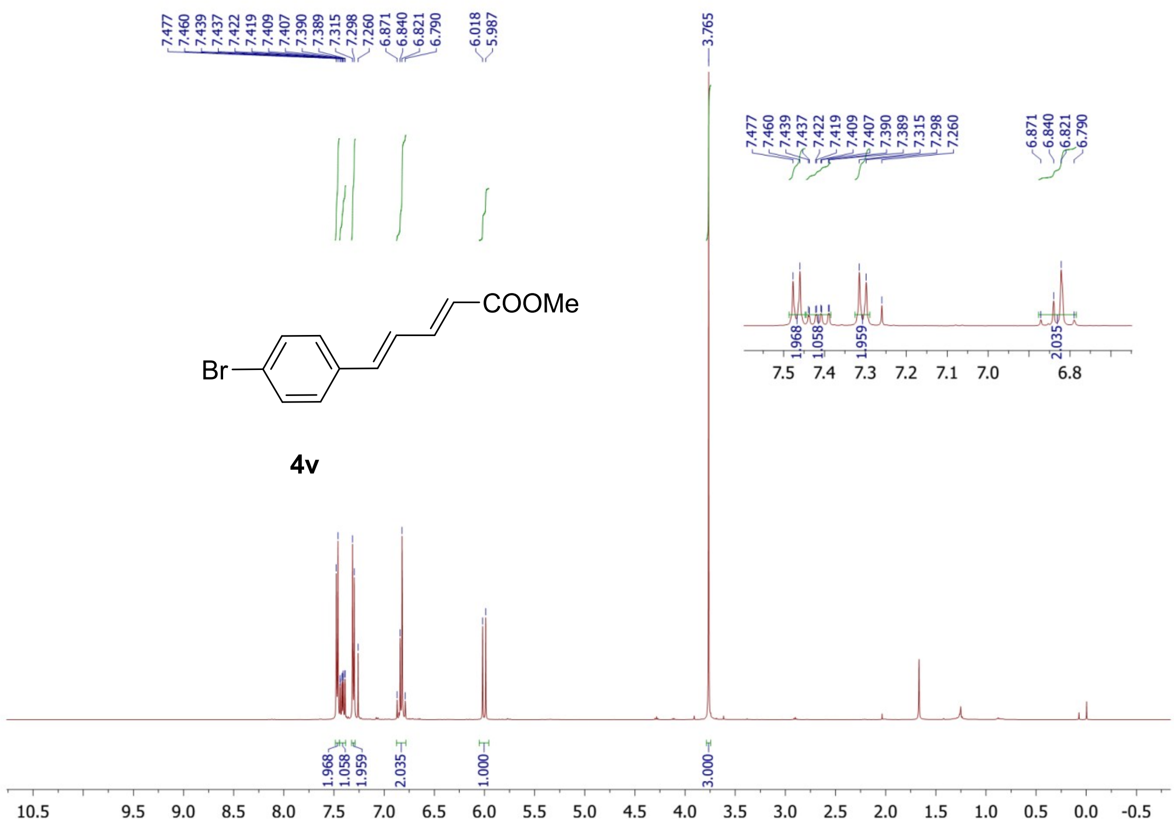
4t, -1H NMR, 500 MHz, $CDCl_3$



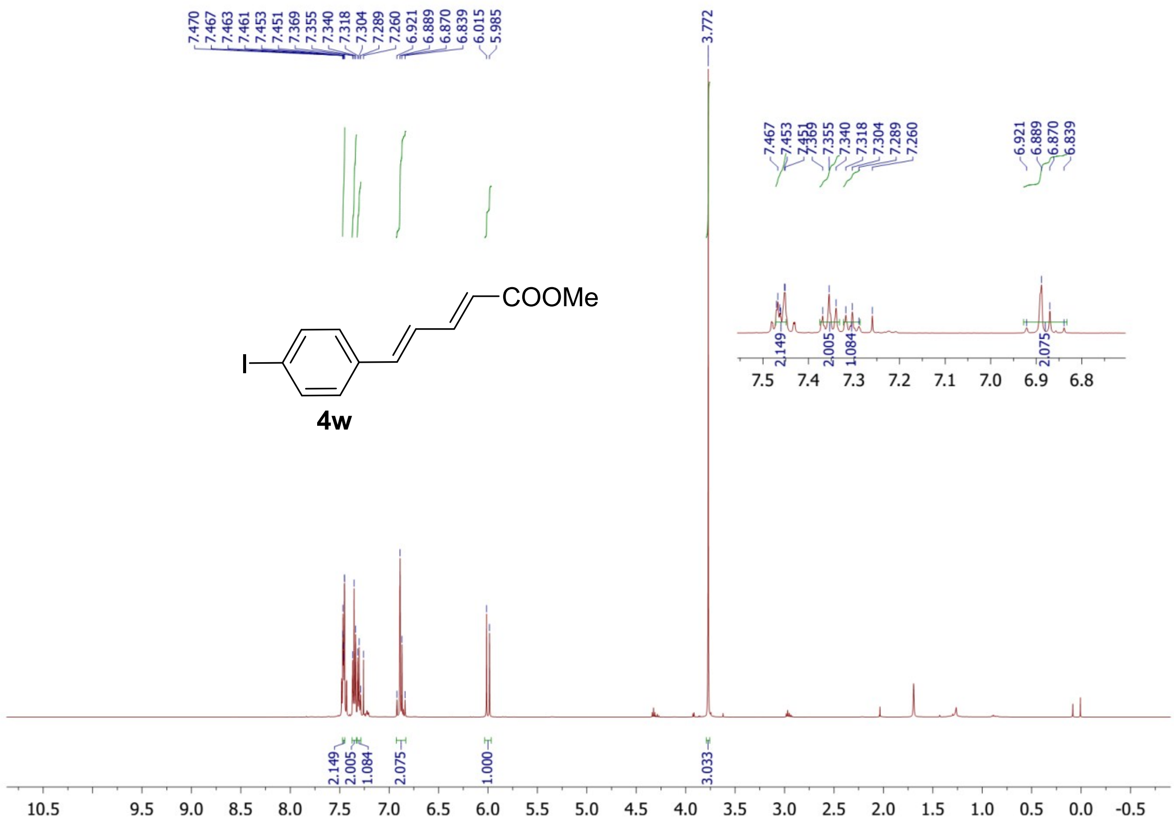
4u, -1H NMR, 500 MHz, $CDCl_3$



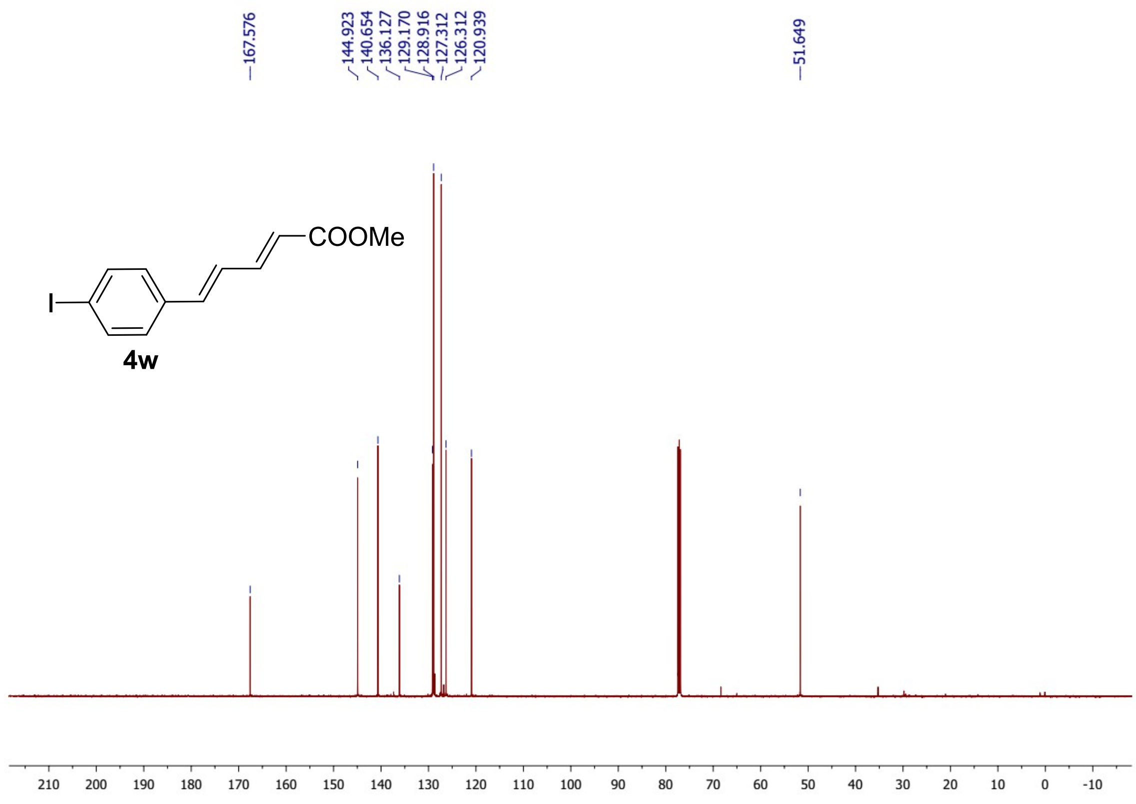
4v, -1H NMR, 500 MHz, $CDCl_3$



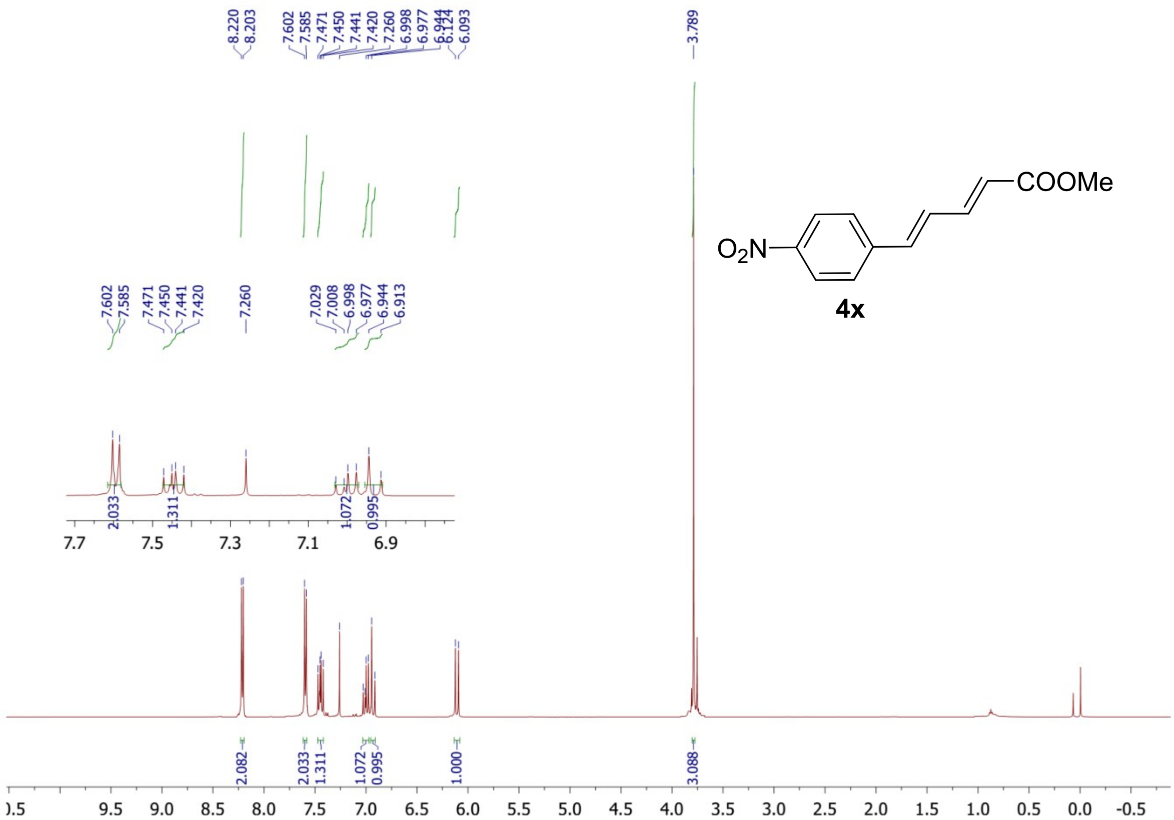
4w, -1H NMR, 500 MHz, $CDCl_3$



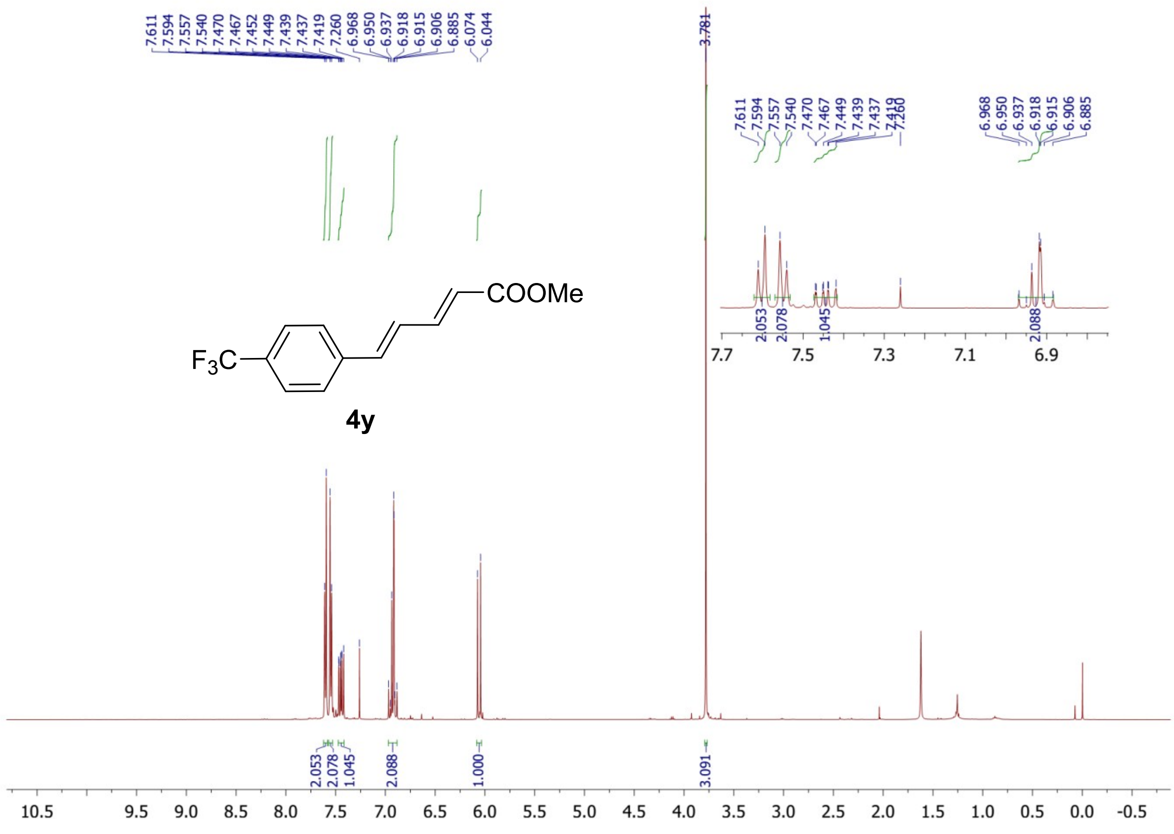
4w, -13C NMR, 126 MHz, $CDCl_3$



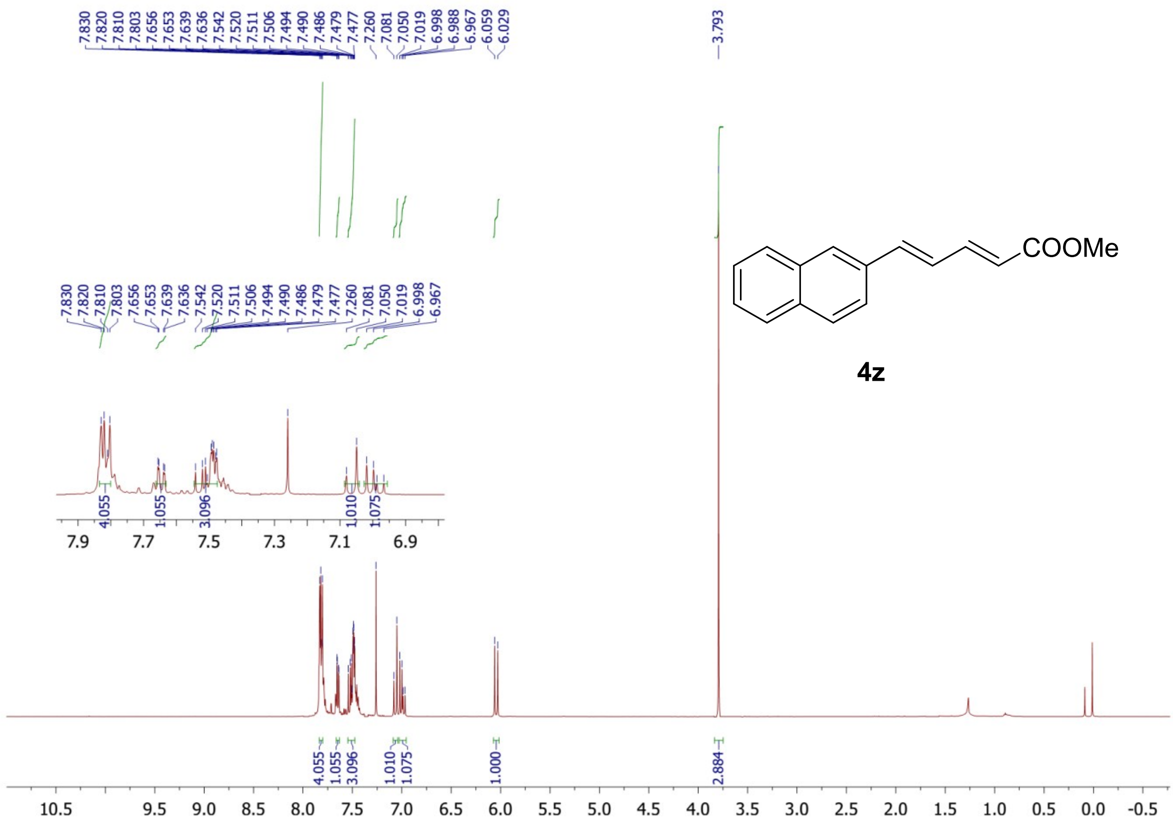
4x, -1H NMR, 500 MHz, $CDCl_3$



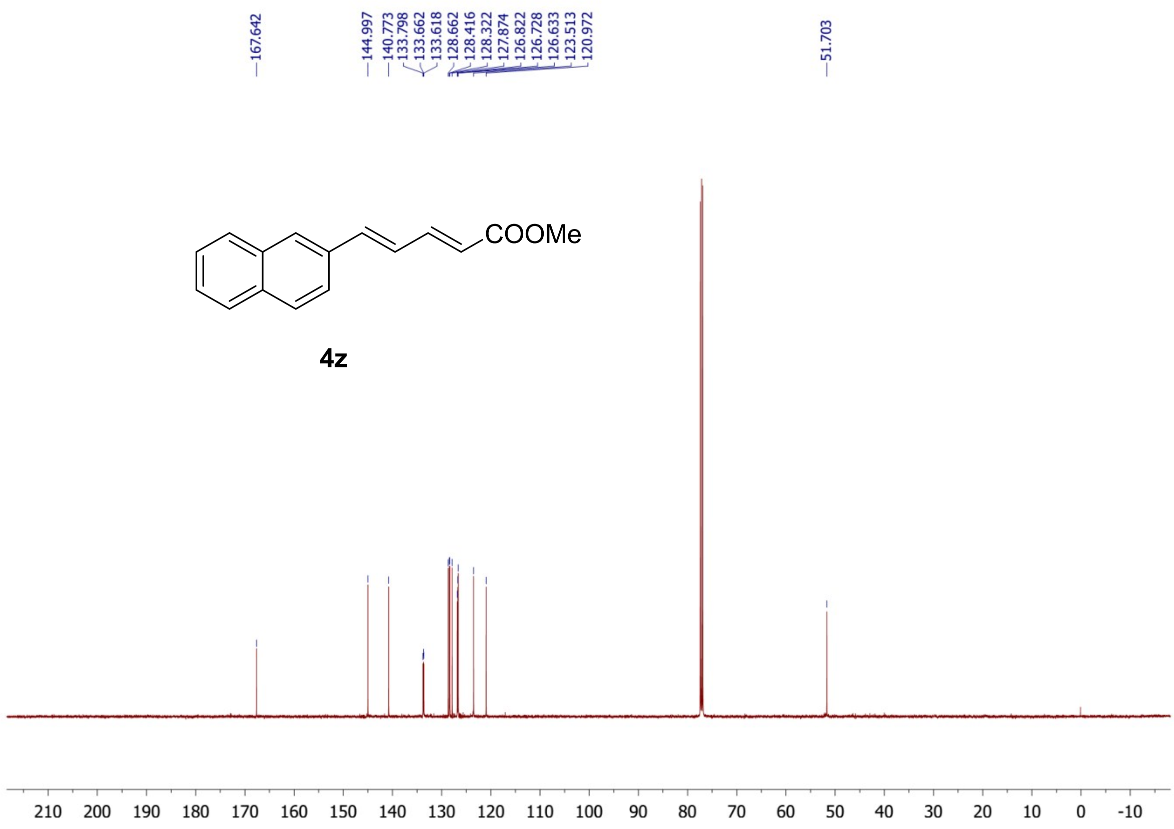
4y, -1H NMR, 500 MHz, $CDCl_3$



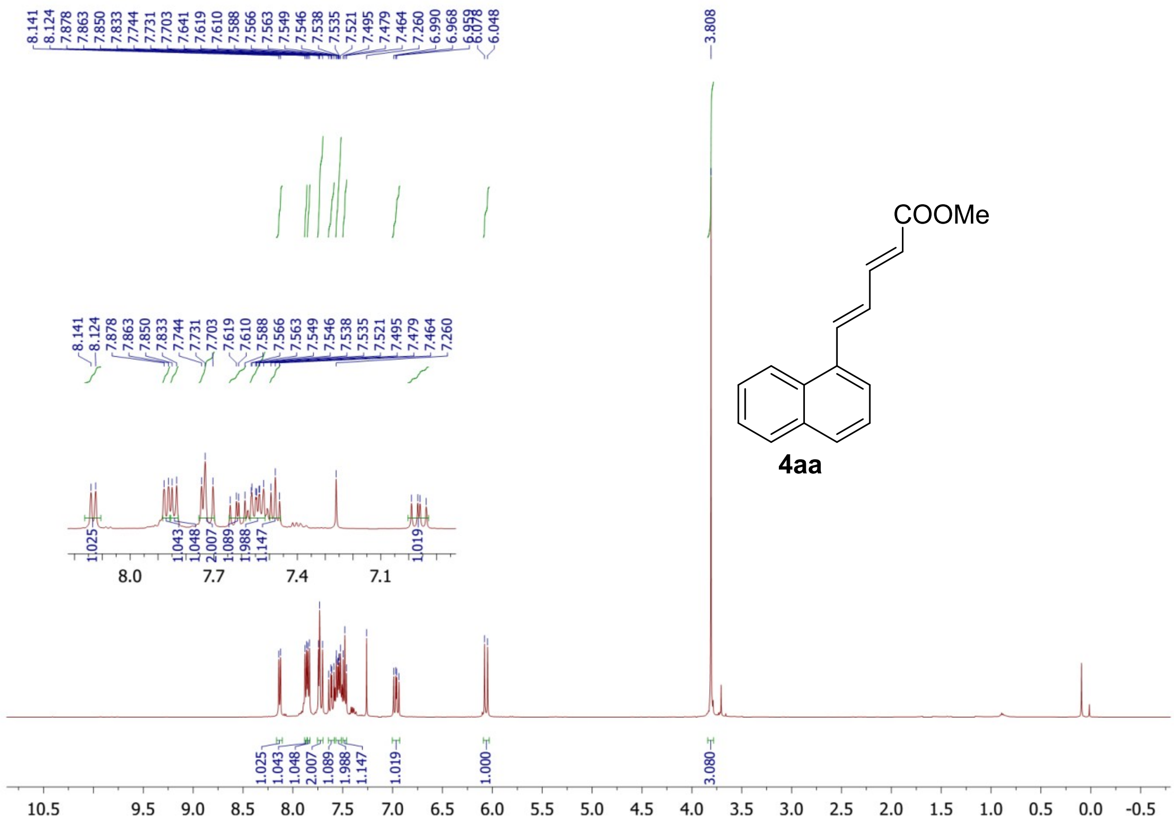
4z, -1H NMR, 500 MHz, $CDCl_3$



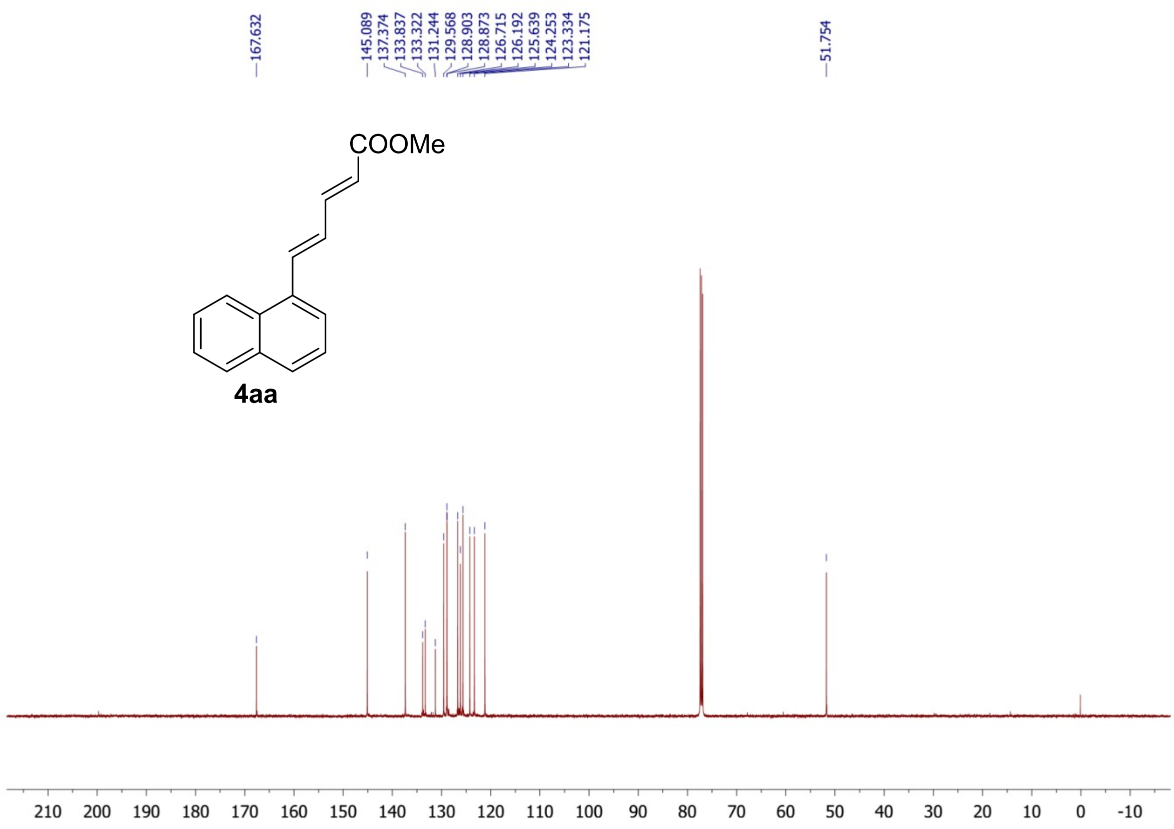
4z, -13C NMR, 126 MHz, $CDCl_3$



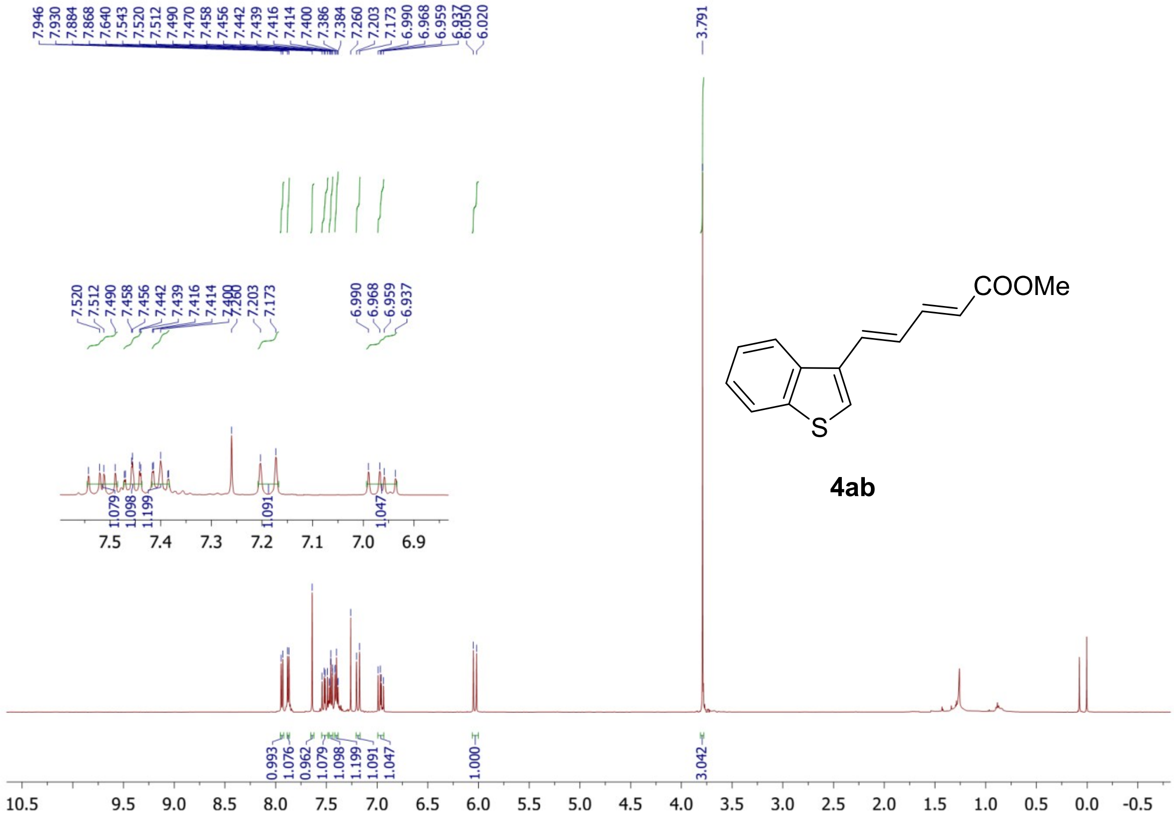
4aa, -1H NMR, 500 MHz, $CDCl_3$



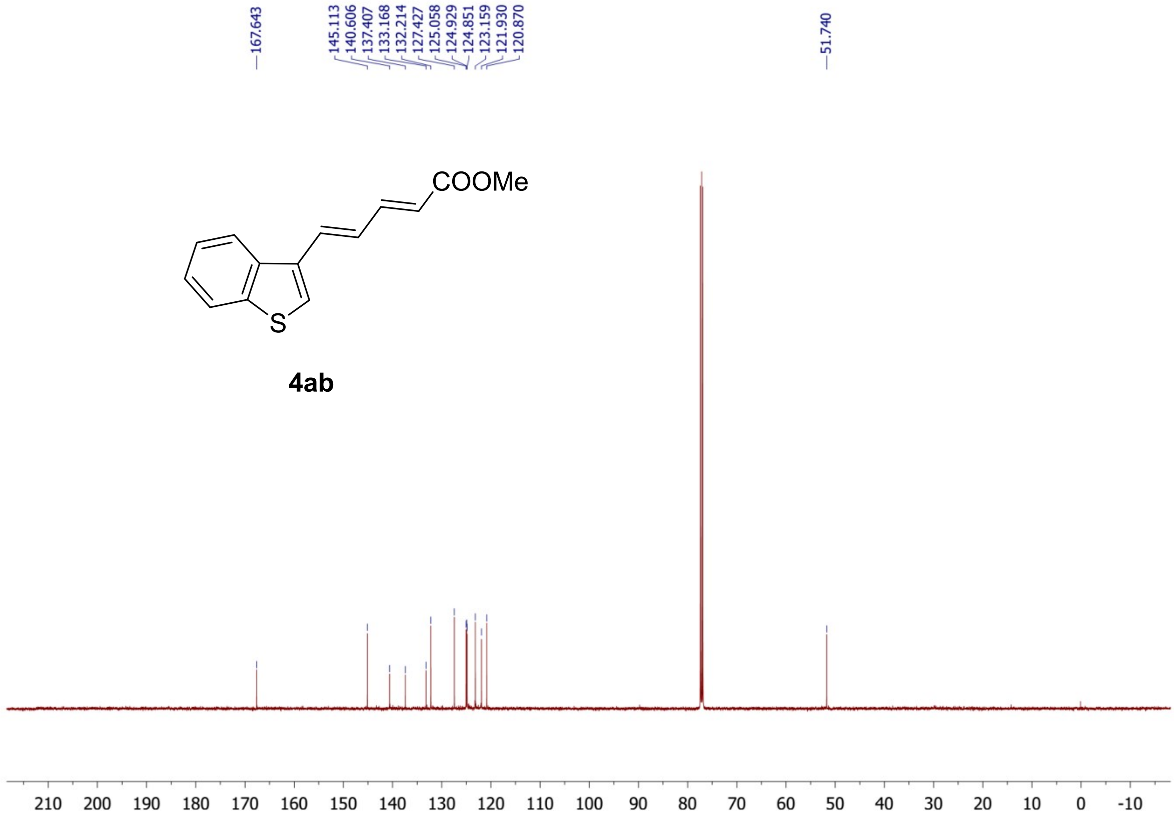
4aa, -13C NMR, 126 MHz, $CDCl_3$



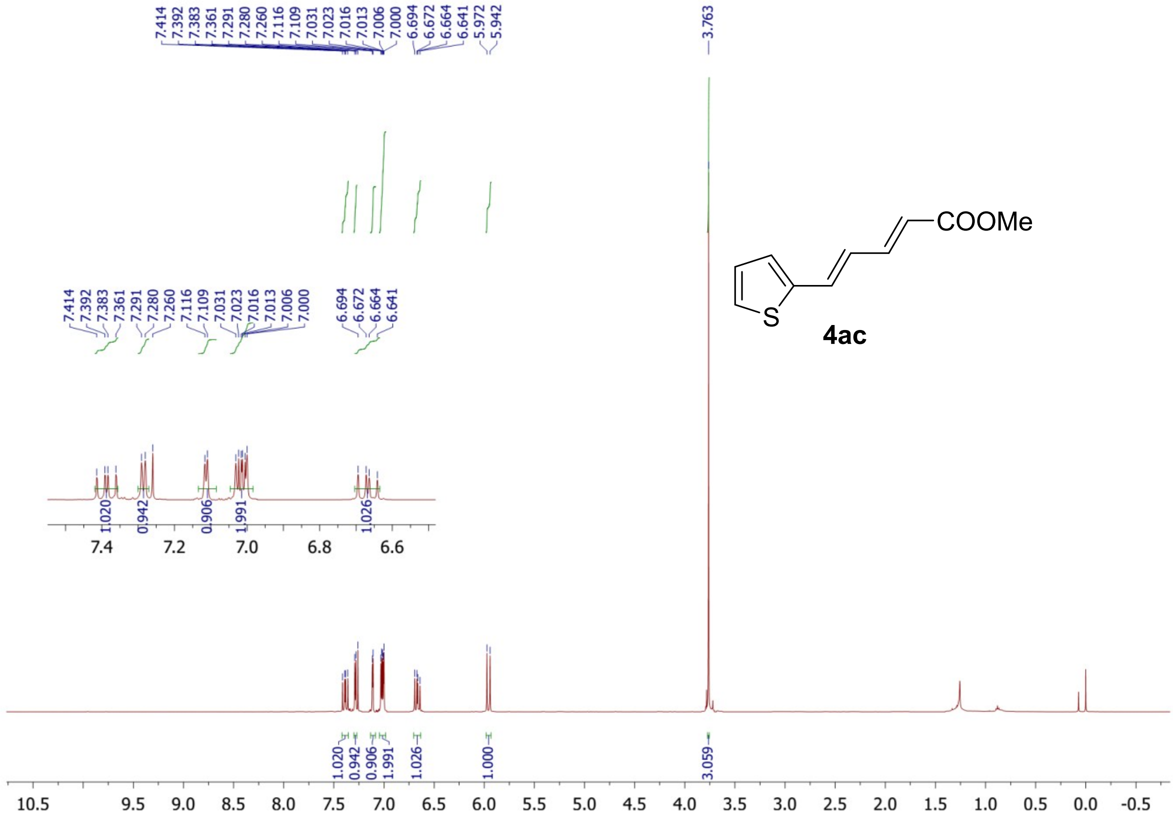
4ab, -1H NMR, 500 MHz, $CDCl_3$



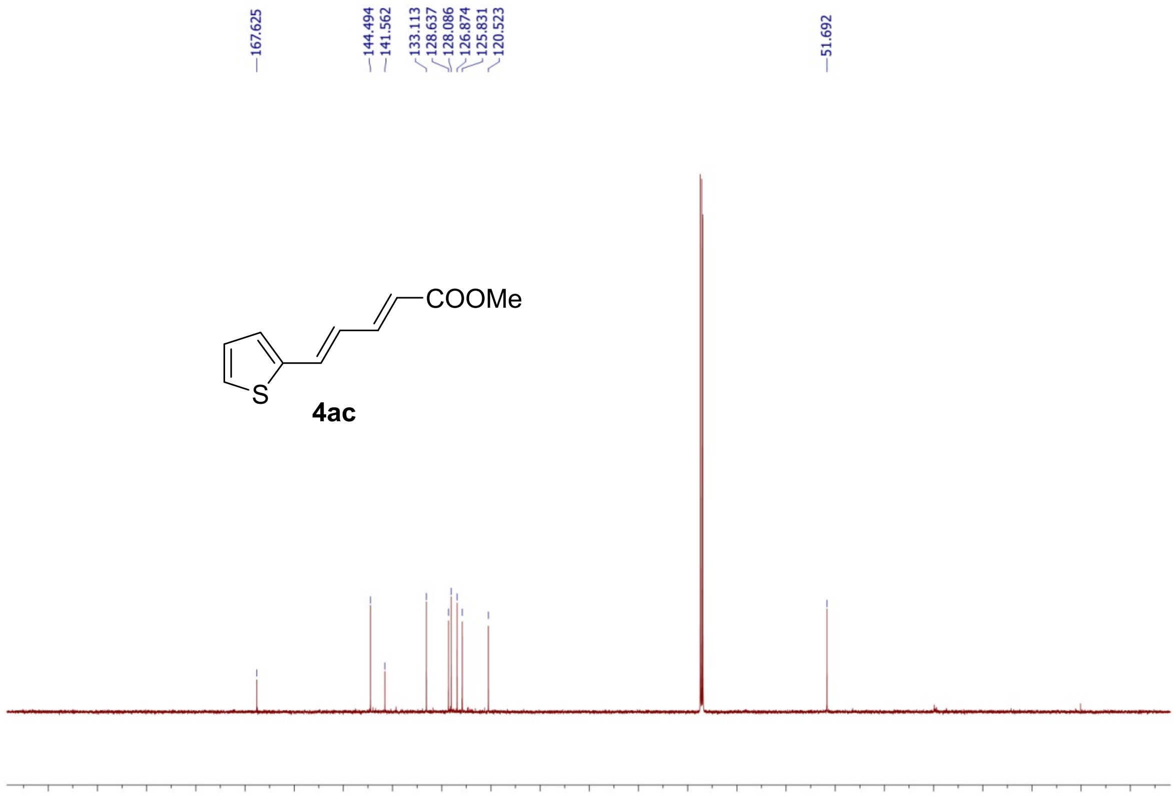
4ab, -13C NMR, 126 MHz, $CDCl_3$



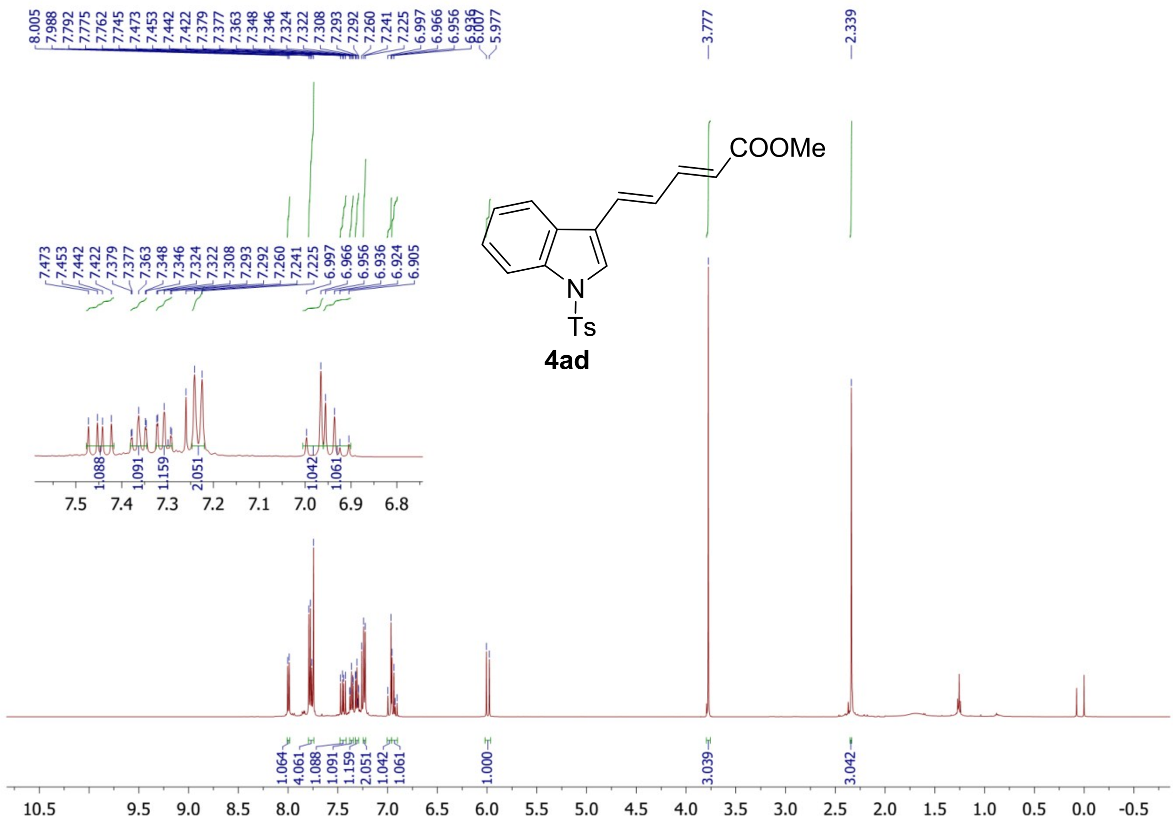
4ac, -1H NMR, 500 MHz, $CDCl_3$



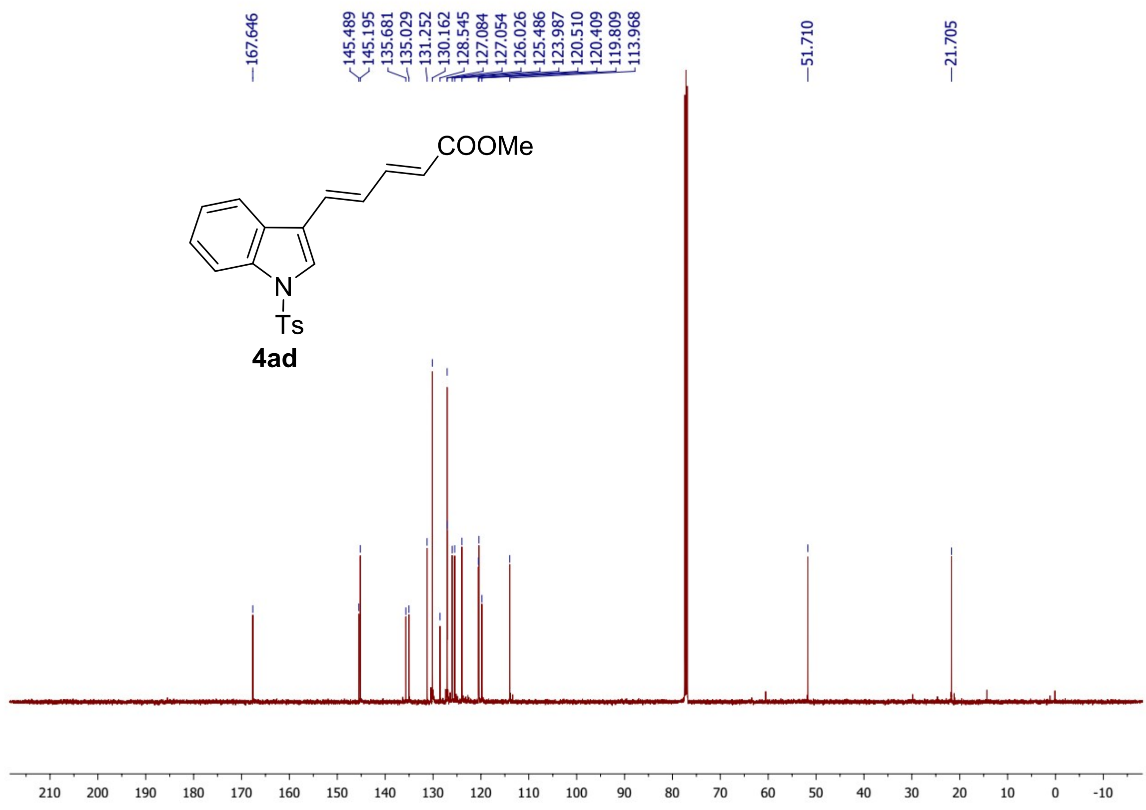
4ac, -13C NMR, 126 MHz, $CDCl_3$



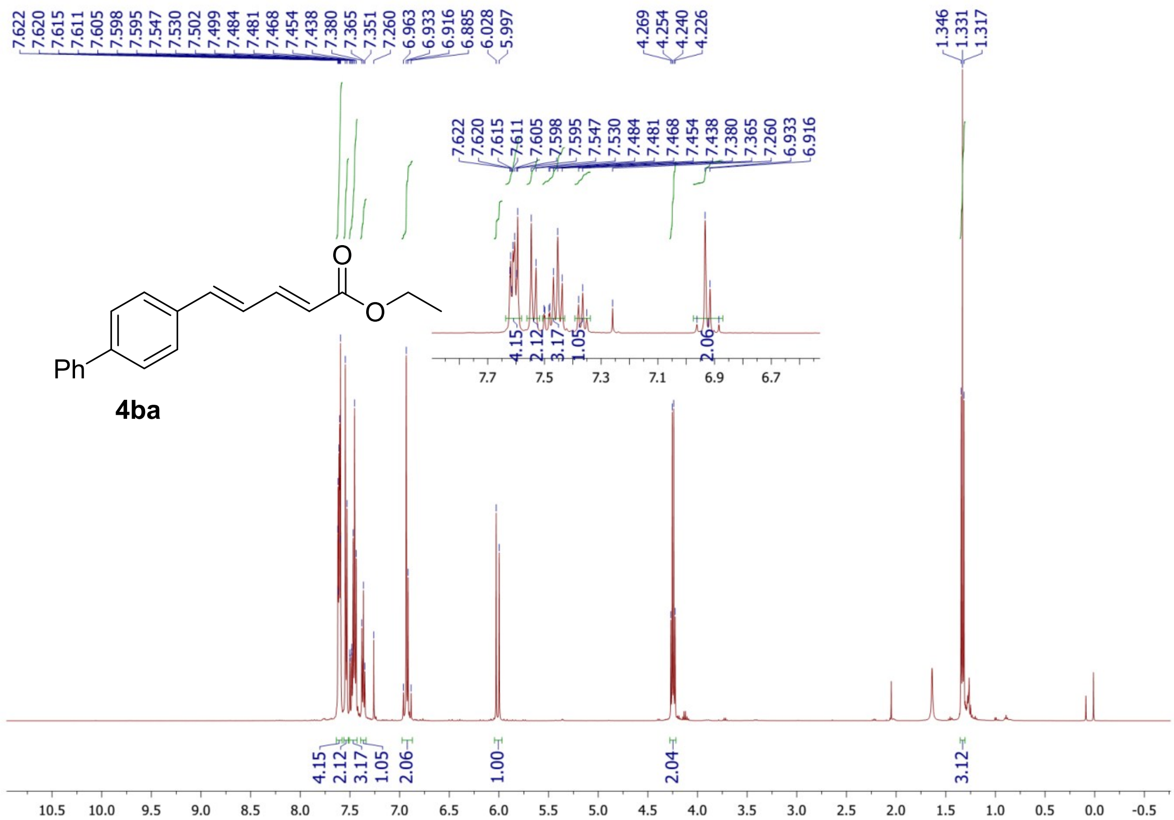
4ad, -1H NMR, 500 MHz, $CDCl_3$



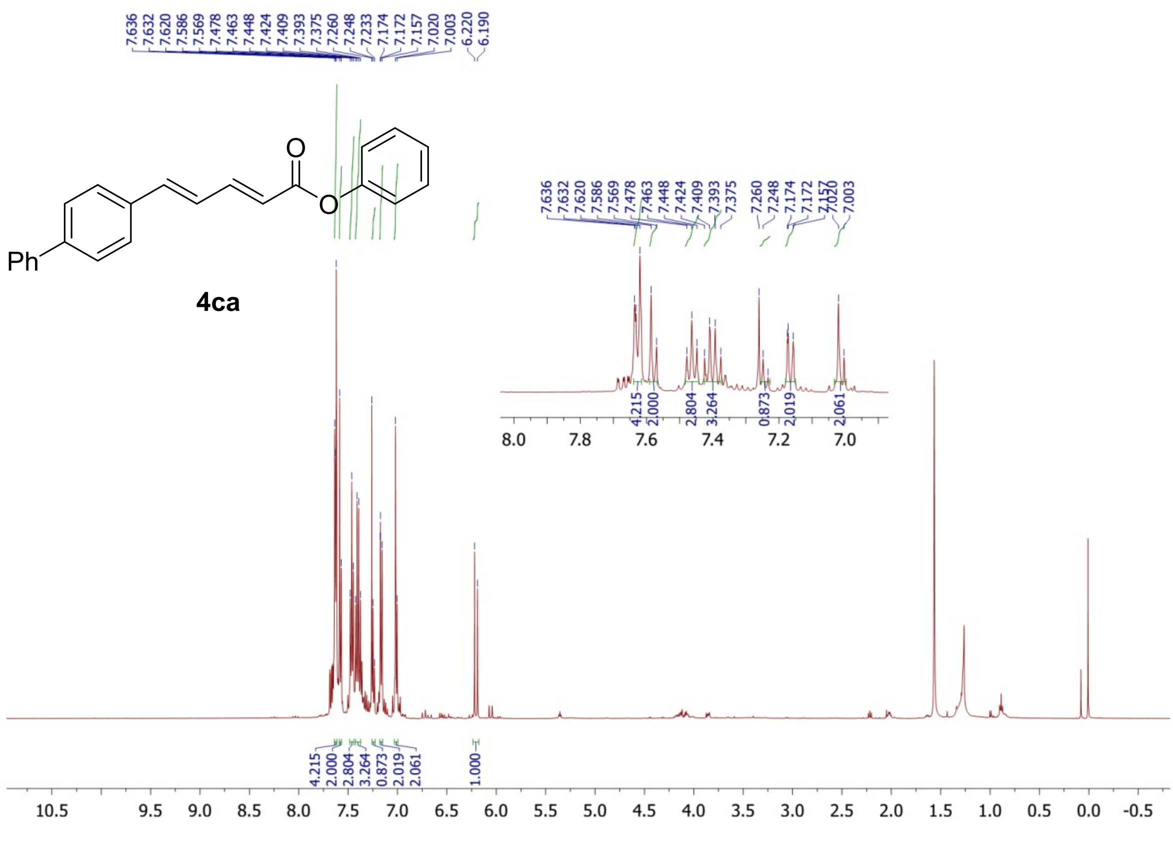
4ad, -13C NMR, 126 MHz, $CDCl_3$



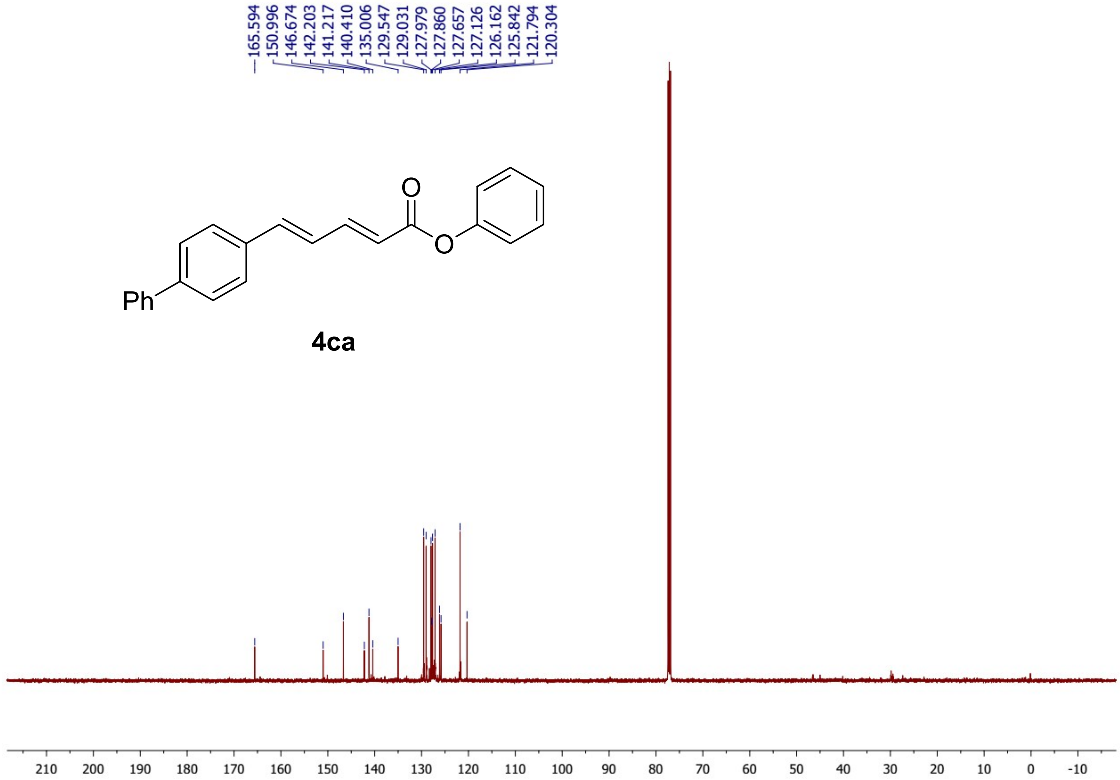
4ba, -1H NMR, 500 MHz, $CDCl_3$



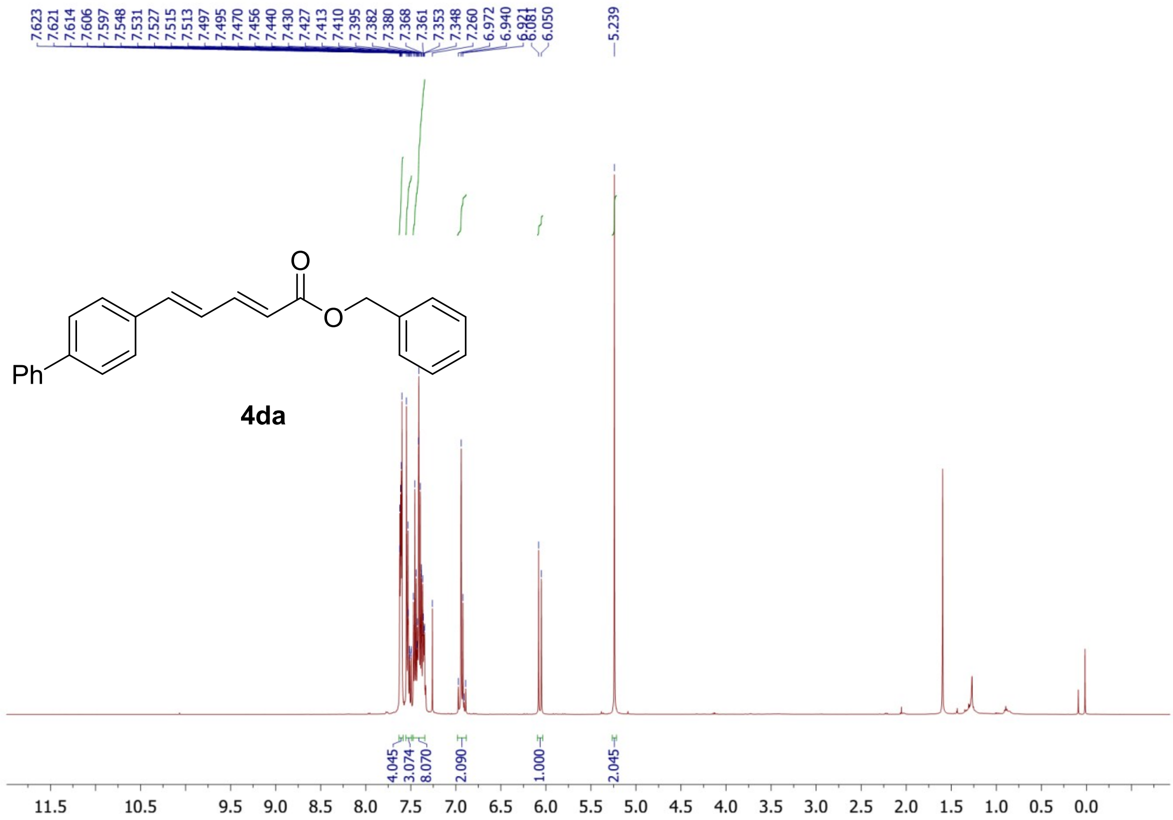
4ca, -1H NMR, 500 MHz, $CDCl_3$



4ca, -13C NMR, 126 MHz, $CDCl_3$



4da, -1H NMR, 500 MHz, $CDCl_3$



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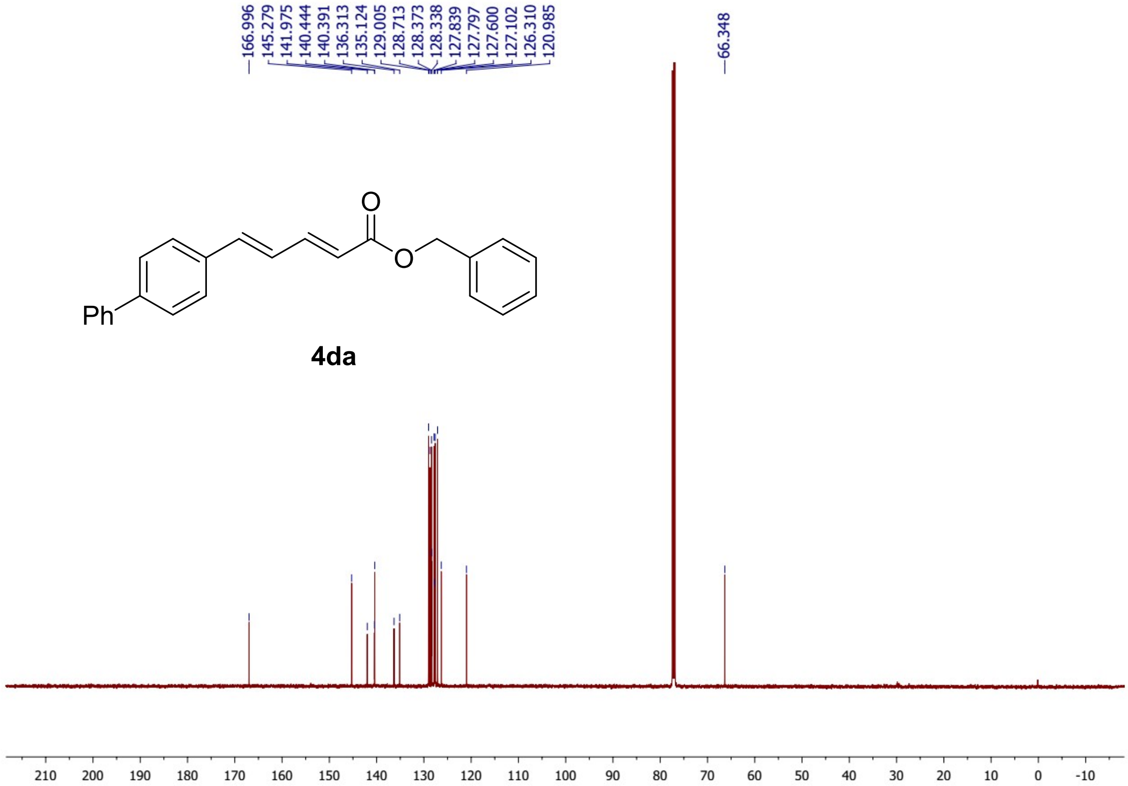

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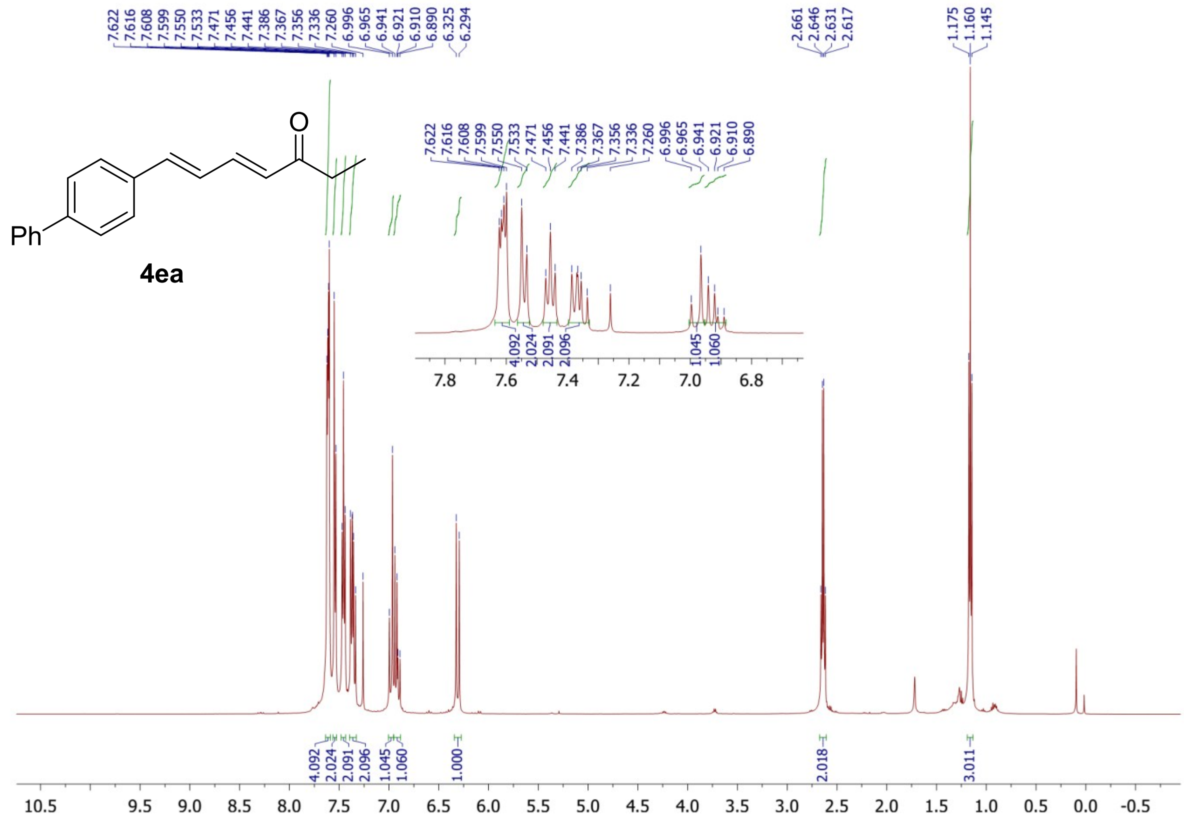

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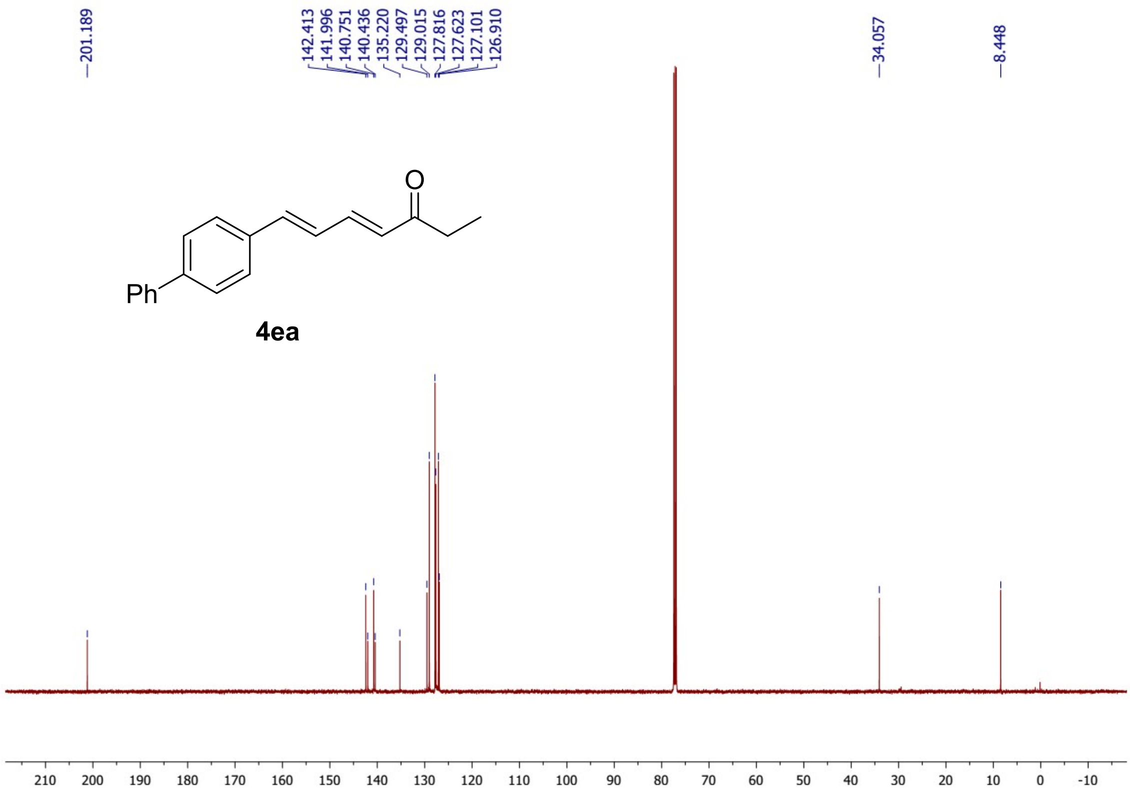
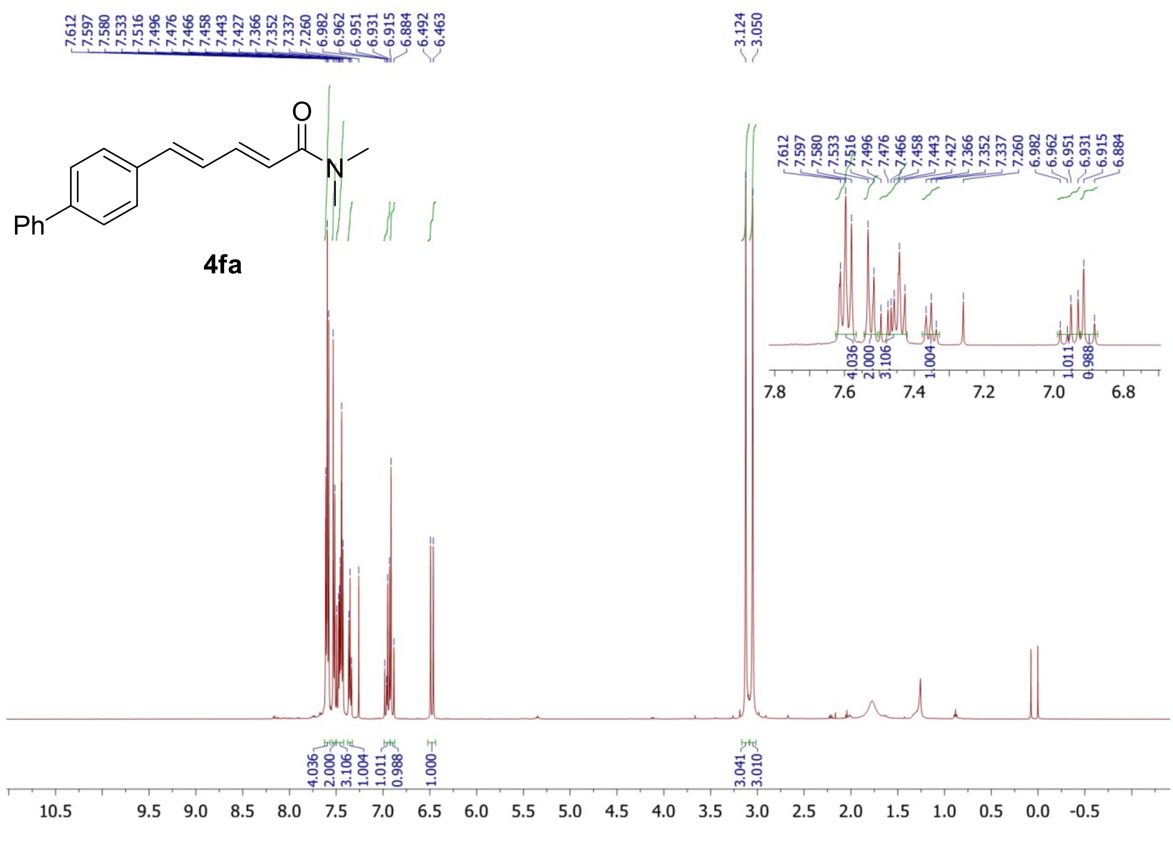


4fa, -1H NMR, 500 MHz, $CDCl_3$



4fa, -13C NMR, 126 MHz, $CDCl_3$