

## Supporting Information

### Copper-catalyzed mild desulfonylation of vinyl sulfonyl molecules

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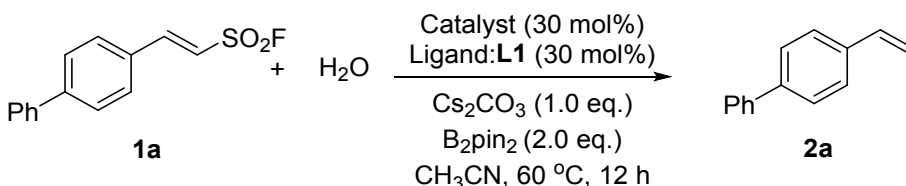
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## 1. General considerations

All reactions were carried out in dried glassware. All reagents were purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  on a 500 or 400 MHz (for  $^1\text{H}$ ), 471 or 376 MHz (for  $^{19}\text{F}$ ), 126 MHz (for  $^{13}\text{C}$ ) spectrometer. All chemical shifts were reported in ppm relative to TMS ( $^1\text{H}$  NMR, 0 ppm) as internal standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5  $\mu\text{m}$ ,  $4.6 \times 150$  mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. 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.

## 2. Optimization of the reaction conditions

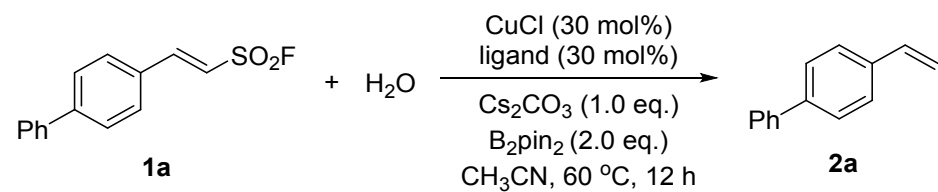
**Table 1. Screening the Catalysts<sup>a</sup>**



Entry	Catalyst (30 mol%)	Yield ( <b>2a</b> , %) <sup>[b]</sup>
1	FeCl <sub>3</sub>	20
2	Fe(acac) <sub>3</sub>	N.D.
3	NiCl <sub>2</sub>	N.D.
4	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	38
5	(CH <sub>3</sub> COO) <sub>2</sub> Cu	63
6	Cu(OTf) <sub>2</sub>	67
7	CuBr	76
8	CuI	70
<b>9</b>	<b>CuCl</b>	<b>77</b>
10 <sup>c</sup>	CuCl	76

<sup>a</sup>General reaction condition: A mixture of (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub>(0.2 mmol, 2.0 eq.), Catalyst (30 mol%), **L1** (30 mol%), Cs<sub>2</sub>CO<sub>3</sub>(0.1 mmol, 1.0 eq.) and CH<sub>3</sub>CN (1.0 mL) were stirred at 60 °C for 12 hours. It is necessary to react for 12 hours, if the reaction time is less than 12 hours, the sulfonyl fluoride cannot be completely converted. <sup>b</sup>HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard (*t*<sub>R</sub> = 4.595min, λ<sub>max</sub> = 276.0 nm, MeOH/H<sub>2</sub>O = 70 : 30 (v / v)). <sup>c</sup>Under argon atmosphere. N. D.: no reaction.

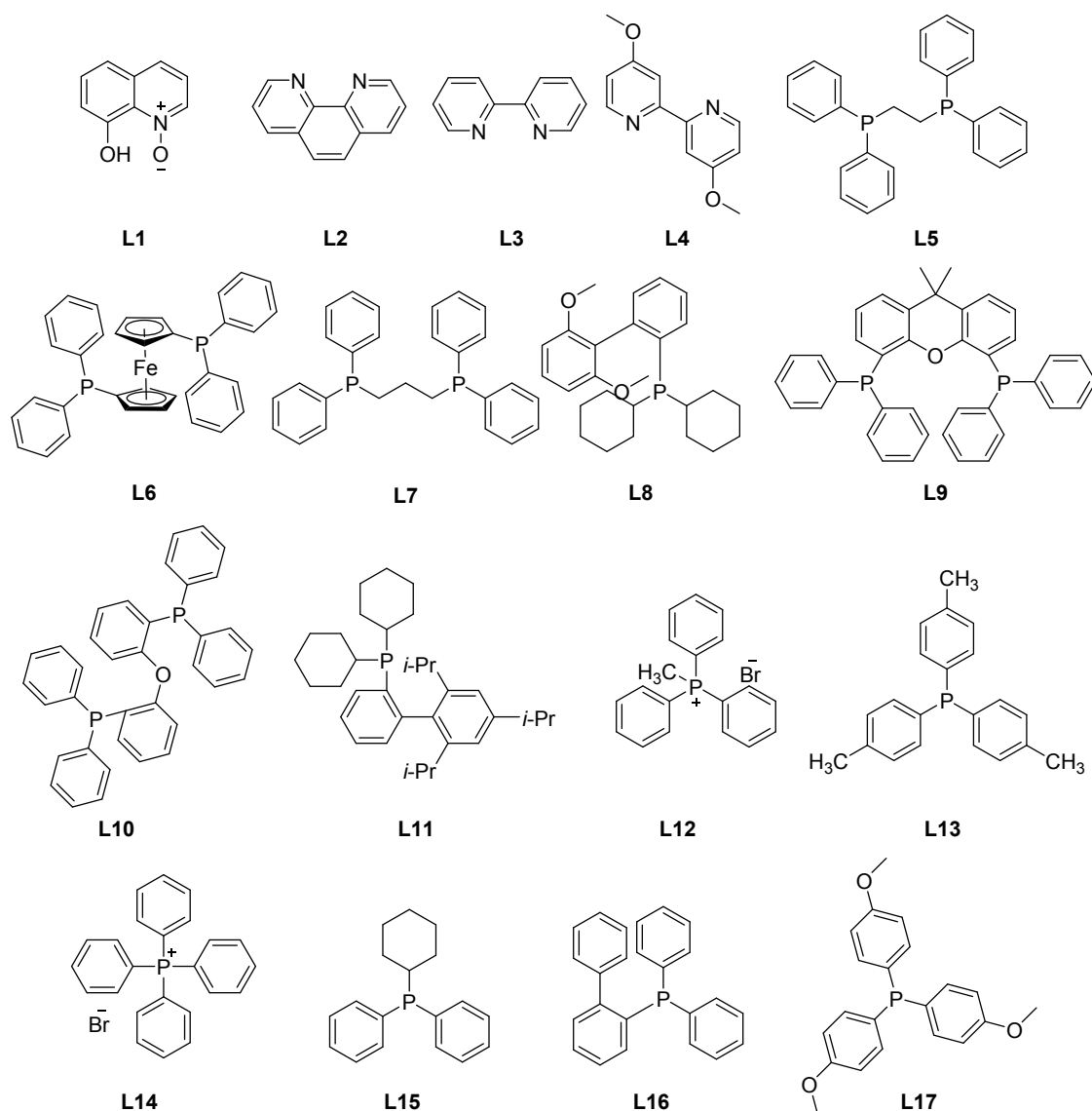
**Table 2. Screening the Ligand<sup>a</sup>**

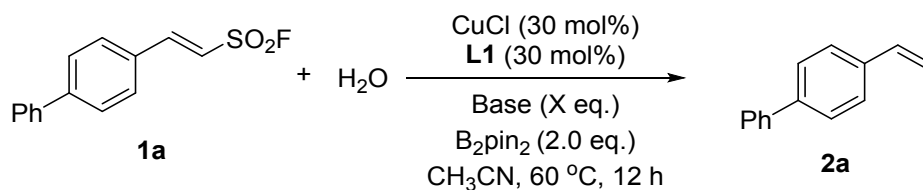


Entry	Ligand (30 mol%)	Yield ( <b>2a</b> , %) <sup>b</sup>
1	/	4
2	<b>L1</b>	77
3	<b>L2</b>	41
4	<b>L3</b>	47
5	<b>L4</b>	44
6	<b>L5</b>	7
7	<b>L6</b>	8
8	<b>L7</b>	14
9	<b>L8</b>	18
10	<b>L9</b>	16
11	<b>L10</b>	23
12	<b>L11</b>	19
13	<b>L12</b>	9
14	<b>L13</b>	29
15	<b>L14</b>	25
16	<b>L15</b>	22
17	<b>L16</b>	6
18	<b>L17</b>	15

<sup>a</sup> General reaction condition: A mixture of (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol, 2.0 eq.), CuCl (30 mol%), Ligand (30 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.1 mmol, 1.0 eq.) and CH<sub>3</sub>CN (1.0 mL) were stirred at 60 °C for 12 hours. <sup>b</sup> HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard (*t<sub>R</sub>* = 4.595 min, λ<sub>max</sub> = 276.0 nm, MeOH/H<sub>2</sub>O = 70 : 30 (v / v)). **L1** is 8-Hydroxyquinoline-N-oxide, **L2** is o-Phenanthroline, **L3** is 2,2'-Dipyridyl, **L4** is

4-Methoxy-2-(4-methoxypyridin-2-yl)pyridine, **L5** is 1,2-Bis(diphenylphosphino)ethane (DPPE), **L6** is 1,1'-Bis(diphenylphosphino)ferrocene (DPPF), **L7** is 1,3-bis(diphenylphosphino) propane (DPPP), **L8** is 2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos), **L9** is 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos), **L10** is Bis(2-diphenylphosphinophenyl)ether (DPEphos), **L11** is 2-(Dicyclohexylphosphino)-2,4,6-Triisopropylbiphenyl (Xphos), **L12** is Methyltriphenylphosphonium bromide, **L13** is Tri-*p*-tolylphosphine, **L14** is tetraphenyl-phosphonium bromide, **L15** is Cyclohexyldiphenylphosphine, **L16** is 2-(Diphenylphosphino)-biphenyl, **L17** is tris(4-methoxyphenyl)phosphine



**Table 3. Screening the Base<sup>a</sup>**

Entry	Base (X eq.)	Yield ( <b>2a</b> , %) <sup>b</sup>
1	DBU (1.0 eq.)	67
2	Pyridine (1.0 eq.)	N.D.
3	K <sub>2</sub> CO <sub>3</sub> (1.0 eq.)	46
4 <sup>c</sup>	K <sub>3</sub> PO <sub>4</sub> (1.0 eq.)	64
5	<i>t</i> -BuONa (1.0 eq.)	26
6	CsF (1.0 eq.)	33
7	Cs <sub>2</sub> CO <sub>3</sub> (1.0 eq.)	77
8	DBU (1.5 eq.)	79
9	K <sub>3</sub> PO <sub>4</sub> (1.5 eq.)	78
<b>10</b>	<b>Cs<sub>2</sub>CO<sub>3</sub> (1.5 eq.)</b>	<b>87</b>
11	Cs <sub>2</sub> CO <sub>3</sub> (2.0 eq.)	87
12	Cs <sub>2</sub> CO <sub>3</sub> (0.5 eq.)	43
13	/	N.D.

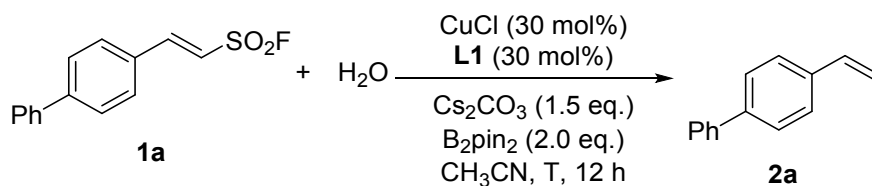
<sup>a</sup>General reaction condition: A mixture of (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol, 2.0 eq.), CuCl (30 mol%), **L1** (30 mol%), Base (X eq.) and CH<sub>3</sub>CN (1.0 mL) were stirred at 60 °C for 12 hours. <sup>b</sup>HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard (*t*<sub>R</sub> = 4.595 min, λ<sub>max</sub> = 276.0 nm, MeOH/H<sub>2</sub>O = 70 : 30 (v / v)).

**Table 4. Screening the solvent<sup>a</sup>**

**1a** + H<sub>2</sub>O  $\xrightarrow[\text{Solvent, 60 } ^\circ\text{C, 12 h}]{\text{CuCl (30 mol\%)}, \text{L1 (30 mol\%)}, \text{Cs}_2\text{CO}_3 \text{ (1.5 eq.)}, \text{B}_2\text{pin}_2 \text{ (2.0 eq.)}}$  **2a**

Entry	Solvent (1 mL)	Yield ( <b>2a</b> , %) <sup>b</sup>
1	CH <sub>3</sub> CN	87
2	Toluene	30
3	Benzene	32
4	EA	47
5	THF	57
6	DMSO	40
7	DMF	60
8	1,4-dioxane	67
9	Acetone	57
10	MeOH	N.D.
11	CH <sub>3</sub> CN with 5% water	53

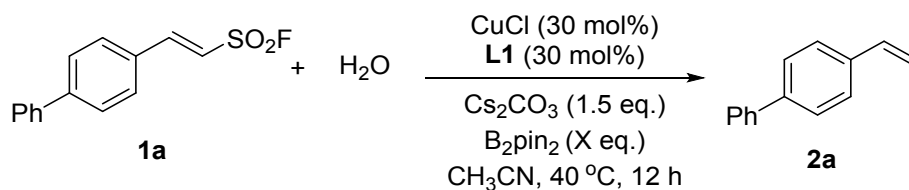
<sup>a</sup>General reaction condition: A mixture of (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub>(0.2 mmol, 2.0 eq.), CuCl (30 mol%), **L1** (30 mol%), Cs<sub>2</sub>CO<sub>3</sub>(0.15 mmol, 1.5 eq.) and Solvent (1.0 mL) were stirred at 60 °C for 12 hours. The regular undried solvent of CH<sub>3</sub>CN containing 0.3% water is sufficient to ensure the reaction proceeds smoothly. <sup>b</sup>HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard (*t*<sub>R</sub> = 4.595 min, λ<sub>max</sub> = 276.0 nm, MeOH/H<sub>2</sub>O = 70 : 30 (v / v)).

**Table 5. Screening the temperature<sup>a</sup>**

Entry	T (°C)	Yield ( <b>2a</b> , %) <sup>b</sup>
1	r.t.	48
2	30	74
<b>3</b>	<b>40</b>	<b>89</b>
4	60	87

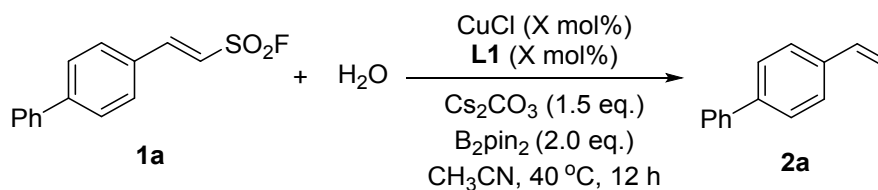
<sup>a</sup>General reaction condition: A mixture of (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub> (0.2 mmol, 2.0 eq.), CuCl (30 mol%), **L1** (30 mol %), Cs<sub>2</sub>CO<sub>3</sub> (0.15 mmol, 1.5 eq.) and CH<sub>3</sub>CN (1.0 mL) were stirred at the corresponding temperature for 12 hours. The regular undried solvent of CH<sub>3</sub>CN containing 0.3% water is sufficient to ensure the reaction proceeds smoothly. <sup>b</sup>HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard (*t*<sub>R</sub> = 4.595 min, λ<sub>max</sub> = 276.0 nm, MeOH/H<sub>2</sub>O = 70 : 30 (v / v)).



**Table 6. Screening the loading of B<sub>2</sub>pin<sub>2</sub><sup>a</sup>**

Entry	B <sub>2</sub> pin <sub>2</sub> (X eq.)	Yield ( <b>2a</b> , %) <sup>b</sup>
1	/	N.D.
2	0.5 eq.	50
3	1.0 eq.	69
4	1.5 eq.	78
<b>5</b>	<b>2.0 eq.</b>	<b>89</b>
6	3.0 eq.	88
7	5.0 eq.	90

<sup>a</sup>General reaction condition: A mixture of (E)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), B<sub>2</sub>pin<sub>2</sub>(X eq.), CuCl (30 mol%), L1 (30 mol%), Cs<sub>2</sub>CO<sub>3</sub>(0.15 mmol, 1.5 eq.) and CH<sub>3</sub>CN (1.0 mL) were stirred at 40 °C for 12 hours. The regular undried solvent of CH<sub>3</sub>CN containing 0.3% water is sufficient to ensure the reaction proceeds smoothly. <sup>b</sup>HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard (t<sub>R</sub> = 4.595 min, λ<sub>max</sub> = 276.0 nm, MeOH/H<sub>2</sub>O = 70 : 30 (v / v)).

**Table 7. Screening the loading of catalyst<sup>a</sup>**

Entry	CuCl (X mol%)	L1 (X mol%)	Yield ( <b>2a</b> , %) <sup>b</sup>
1	3	3	48
2	5	5	89
3	10	10	89
4	20	20	90
5	30	30	90
6	50	50	91

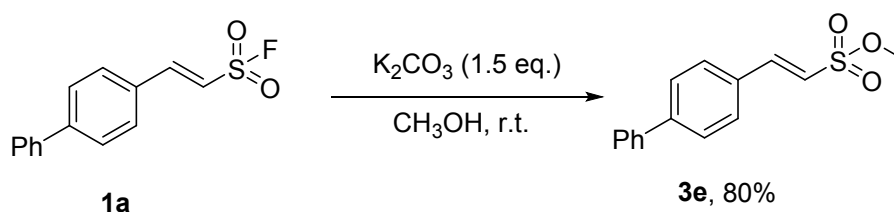
<sup>a</sup>General reaction condition: A mixture of (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 0.1 mmol),  $\text{B}_2\text{pin}_2$  (0.2 mmol, 2.0 eq.),  $\text{CuCl}$  (X mol%), **L1** (X mol%),  $\text{Cs}_2\text{CO}_3$  (0.15 mmol, 1.5 eq.) and  $\text{CH}_3\text{CN}$  (1.0 mL) were stirred at  $40\text{ }^\circ\text{C}$  for 12 hours. The regular undried solvent of  $\text{CH}_3\text{CN}$  containing 0.3% water is sufficient to ensure the reaction proceeds smoothly. <sup>b</sup>HPLC yields using the pure 4-vinyl-1,1'-biphenyl (**2a**, 0.1 mmol) as the external standard ( $t_R = 4.595\text{ min}$ ,  $\lambda_{\text{max}} = 276.0\text{ nm}$ ,  $\text{MeOH}/\text{H}_2\text{O} = 70 : 30\text{ (v / v)}$ ).

### 3. General procedure

#### 3.1 Preparation of Substrates, (Hetero)arylethenesulfonyl Fluoride 1

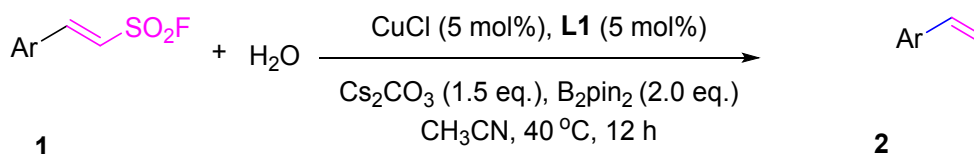
**1a-1y**, **1aa**, **1ac**, **1ae**, **5a**, **5b**, and **5c** were prepared according to the literature.<sup>1</sup> **1z**, **1ab**, and **1ad** were prepared according to the literature.<sup>2</sup> **3a** and **3b** were prepared according to the literature.<sup>3</sup> **3c** were prepared according to the literature.<sup>4</sup> **3d** were prepared according to the literature.<sup>5</sup> **3f** were prepared according to the literature.<sup>6</sup> **1f** and **1g** were prepared according to the literature.<sup>7</sup> All homemade starting materials are identical to those reported regarding the <sup>1</sup>H and <sup>13</sup>C NMR and melting points (if applicable).

#### 3.2 Procedure for 3e



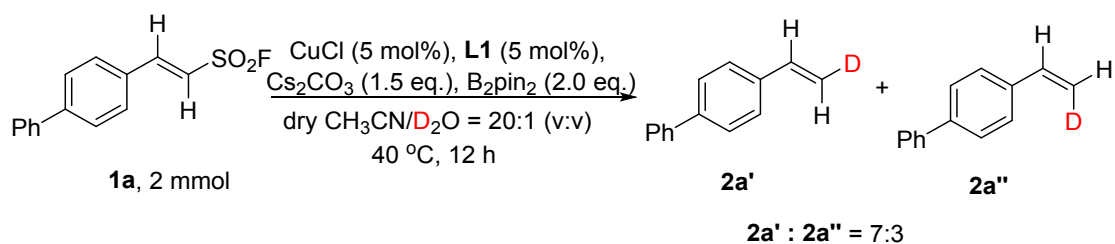
(*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 5.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.5 mmol), and CH<sub>3</sub>OH (30 mL) were added to an oven-dried reaction tube (50 mL) and stirred at room temperature for 12 h before concentrating under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **3e**.

#### 3.3 Procedure for vinyl sulfonyl fluorides to terminal olefins



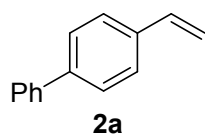
Vinyl sulfonyl fluoride (**1**, 1.0 mmol, 1.0 eq.), CuCl (5.0 mg, 5 mol%), **L1** (8.0 mg, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (488.7 mg, 1.5 mmol, 1.5 eq.), B<sub>2</sub>pin<sub>2</sub> (507.8 mg, 2.0 mmol, 2.0 eq.) and CH<sub>3</sub>CN (10.0 mL) were added to an oven-dried reaction tube (50 mL) and stirred at 40 °C for 12 h. After completion of the reaction, the resulting reaction mixture was diluted with water and extracted with EtOAc (3×20 mL) and the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness. The residue was purified by column chromatography on silica gel to afford the desired olefins

### 3.4 Deuterium labeling experiment

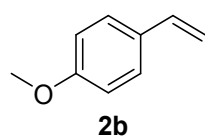


(*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonyl fluoride (**1a**, 2.0 mmol), CuCl (10 mg, 5 mol%), **L1** (16 mg, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (977.4 mg, 3.0 mmol, 1.5 eq.), B<sub>2</sub>pin<sub>2</sub> (1.02 g, 4.0 mmol, 2.0 eq.), dry CH<sub>3</sub>CN (20.0 mL), and D<sub>2</sub>O (1 mL) were added to an oven-dried reaction tube (50 mL) and stirred at 40 °C for 12 h. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.63-7.58 (m, 4H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.47-7.44 (m, 2H), 7.38-7.34 (m, 1H), 6.78 (d, *J* = 17.7 Hz, 1H), 5.80 (d, *J* = 17.5 Hz, 0.70H), 5.28 (d, *J* = 10.8 Hz, 0.30H). Deuterium incorporation is 90%, and the ratio of **2a'** and **2a''** is 7:3.

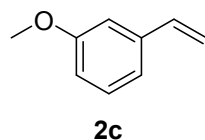
#### 4. Product Characterization



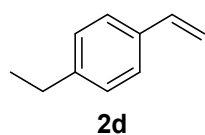
4-Vinyl-1,1'-biphenyl (**2a**). White solid (151 mg from **1a**, isolated yield 84%). HPLC yield 89% (using 4-vinyl-1,1'-biphenyl (**2a**) ( $t_R = 4.595$  min,  $\lambda_{max} = 276.0$  nm, MeOH/H<sub>2</sub>O = 70: 30 (v / v)) as the external standard). The NMR data is identical to that reported in literature.<sup>8</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.64-7.59 (m, 4H), 7.51 (d,  $J = 8.2$  Hz, 2H), 7.46 (t,  $J = 7.4$  Hz, 2H), 7.37 (t,  $J = 7.3$  Hz, 1H), 6.79 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.82 (d,  $J = 17.6$  Hz, 1H), 5.30 (d,  $J = 10.9$  Hz, 1H).



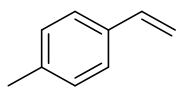
1-Methoxy-4-vinylbenzene (**2b**). Colorless liquid. (103 mg from **1b**, isolated yield 77%). HPLC yield 90% (using 1-methoxy-4-vinylbenzene (**2b**) ( $t_R = 4.354$  min,  $\lambda_{max} = 257.1$  nm, MeOH/H<sub>2</sub>O = 80: 20 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.40 (d,  $J = 8.7$  Hz, 2H), 6.92 (d,  $J = 8.7$  Hz, 2H), 6.73 (dd,  $J = 17.7$  Hz, 11.0 Hz, 1H), 5.67 (d,  $J = 17.6$  Hz, 1H), 5.19 (d,  $J = 10.8$  Hz, 1H), 3.84 (s, 3H).



1-Methoxy-3-vinylbenzene (**2c**). Colorless liquid. (118 mg from **1c**, isolated yield 88%). The NMR data is identical to that reported in literature.<sup>10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.26 (t,  $J = 7.8$  Hz, 1H), 7.03 (d,  $J = 7.7$  Hz, 1H), 6.97 (t,  $J = 2.1$  Hz, 1H), 6.83 (dd,  $J = 8.1$  Hz, 2.3 Hz, 1H), 6.71 (dd,  $J = 17.7$  Hz, 11.0 Hz, 1H), 5.76 (d,  $J = 17.5$  Hz, 1H), 5.27 (d,  $J = 10.8$  Hz, 1H), 3.84 (s, 3H).

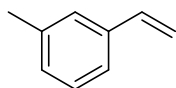


1-Ethyl-4-vinylbenzene (**2d**). Colorless liquid. (108 mg from **1d**, isolated yield 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.36 (d,  $J = 8.1$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 6.73 (dd,  $J = 17.7$  Hz, 10.8 Hz, 1H), 5.73 (dd,  $J = 17.6$  Hz, 0.8 Hz, 1H), 5.21 (dd,  $J = 11.0$  Hz, 0.8 Hz, 1H), 2.67 (q,  $J = 7.6$  Hz, 2H), 1.26 (t,  $J = 7.7$  Hz, 3H). <sup>13</sup>C (CDCl<sub>3</sub>, 126 MHz)  $\delta$  144.2, 136.9, 135.2, 128.2, 126.3, 112.9, 28.7, 15.7. ESI-MS HRMS calculated for C<sub>10</sub>H<sub>13</sub> [M+H]<sup>+</sup> 133.1012, found: 133.1008.



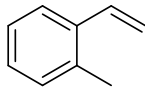
**2e**

1-Methyl-4-vinylbenzene (**2e**). Colorless liquid. (98 mg from **1e**, isolated yield 83%). HPLC yield 90% (using 1-methyl-4-vinylbenzene (**2e**) ( $t_R = 3.372$  min,  $\lambda_{max} = 251.2$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard). The NMR data is identical to that reported in literature.<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.36 (d,  $J = 8.1$  Hz, 2H), 7.18 (d,  $J = 8.1$  Hz, 2H), 6.74 (dd,  $J = 17.7$  Hz, 10.8 Hz, 1H), 5.75 (d,  $J = 17.6$  Hz, 1H), 5.24 (d,  $J = 11.0$  Hz, 1H), 2.39 (s, 3H).



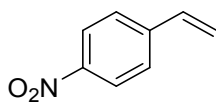
**2f**

1-Methyl-3-vinylbenzene (**2f**). Colorless liquid. (97 mg from **1f**, isolated yield 82%). HPLC yield 92% (using 1-methyl-3-vinylbenzene (**2f**) ( $t_R = 3.372$  min,  $\lambda_{max} = 248.8$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard). The NMR data is identical to that reported in literature.<sup>11</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.22-7.20 (m, 3H), 7.07-7.06 (m, 1H), 6.68 (dd,  $J = 17.6$  Hz, 10.9 Hz, 1H), 5.72 (d,  $J = 17.7$  Hz, 1H), 5.21 (d,  $J = 10.9$  Hz, 1H), 2.34 (s, 3H).



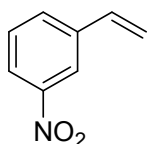
**2g**

1-Methyl-2-vinylbenzene (**2g**). Colorless liquid. (95 mg from **1g**, isolated yield 80%). HPLC yield 93% (using 1-methyl-2-vinylbenzene (**2g**) ( $t_R = 3.391$  min,  $\lambda_{max} = 270.1$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard). The NMR data is identical to that reported in literature.<sup>11</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.40-7.38 (m, 1H), 7.10-7.04 (m, 3H), 6.86 (dd,  $J = 17.4$  Hz, 11.0 Hz, 1H), 5.55 (dd,  $J = 17.4$  Hz, 1.1 Hz, 1H), 5.20 (dd,  $J = 11.0$  Hz, 1.0 Hz, 1H), 2.26 (s, 3H).



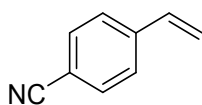
**2h**

1-Nitro-4-vinylbenzene (**2h**). Colorless liquid. (84 mg from **1h**, isolated yield 56%). The NMR data is identical to that reported in literature.<sup>12</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.19 (d,  $J = 8.9$  Hz, 2H), 7.54 (d,  $J = 8.9$  Hz, 2H), 6.79 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.93 (d,  $J = 17.6$  Hz, 1H), 5.50 (d,  $J = 10.9$  Hz, 1H).



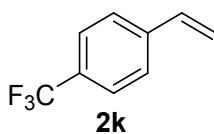
**2i**

1-Nitro-3-vinylbenzene (**2i**). Colorless liquid. (82 mg from **1i**, isolated yield 55%). The NMR data is identical to that reported in literature.<sup>13</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.24 (s, 1H), 8.10 (dd,  $J = 8.1$  Hz, 1.0 Hz, 1H), 7.70 (d,  $J = 7.8$  Hz, 1H), 7.49 (t,  $J = 8.1$  Hz, 1H), 6.77 (dd,  $J = 17.5$  Hz, 11.0 Hz, 1H), 5.89 (d,  $J = 17.5$  Hz, 1H), 5.44 (d,  $J = 10.8$  Hz, 1H).



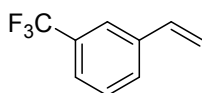
**2j**

4-Vinylbenzotrile (**2j**). Colorless liquid. (90 mg from **1j**, isolated yield 70%). HPLC yield 95% (using 4-vinylbenzotrile (**2j**) ( $t_R = 3.000$  min,  $\lambda_{max} = 264.2$  nm, MeOH/H<sub>2</sub>O = 80: 20 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>11</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.62 (d,  $J = 8.3$  Hz, 2H), 7.49 (d,  $J = 8.3$  Hz, 2H), 6.73 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.88 (d,  $J = 17.5$  Hz, 1H), 5.45 (d,  $J = 10.8$  Hz, 1H).



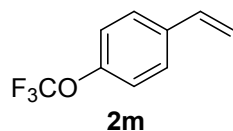
**2k**

1-(Trifluoromethyl)-4-vinylbenzene(**2k**). Colorless liquid. (129 mg from **1k**, isolated yield 75%). HPLC yield 94% (using 1-(trifluoromethyl)-4-vinylbenzene (**2k**) ( $t_R = 3.595$  min,  $\lambda_{max} = 258.7$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>11</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.59 (d,  $J = 8.2$  Hz, 2H), 7.51 (d,  $J = 8.2$  Hz, 2H), 6.76 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.86 (d,  $J = 17.6$  Hz, 1H), 5.40 (d,  $J = 11.0$  Hz, 1H).

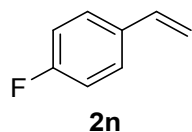


**2l**

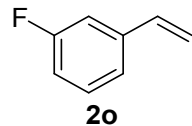
1-(Trifluoromethyl)-3-vinylbenzene (**2l**). Colorless liquid. (124 mg from **1l**, isolated yield 72%). HPLC yield 90% (using 1-(trifluoromethyl)-4-vinylbenzene (**2l**) ( $t_R = 3.557$  min,  $\lambda_{max} = 260.6$  nm, MeOH/H<sub>2</sub>O = 80: 20 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.67 (s, 1H), 7.59 (d,  $J = 7.8$  Hz, 1H), 7.52 (d,  $J = 7.8$  Hz, 1H), 7.45 (t,  $J = 7.7$  Hz, 1H), 6.76 (dd,  $J = 17.5$  Hz, 10.9 Hz, 1H), 5.84 (d,  $J = 17.6$  Hz, 1H), 5.38 (d,  $J = 11.0$  Hz, 1H).



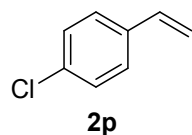
1-(Trifluoromethoxy)-4-vinylbenzene (**2m**). Colorless liquid. (154 mg from **1m**, isolated yield 82%). HPLC yield 94% (using 1-(trifluoromethoxy)-4-vinylbenzene (**2m**) ( $t_R = 4.595$  min,  $\lambda_{max} = 276.0$  nm, MeOH/H<sub>2</sub>O = 70: 30 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>14</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.43 (d,  $J = 8.7$  Hz, 2H), 7.18 (d,  $J = 8.1$  Hz, 2H), 6.71 (dd,  $J = 17.6$  Hz, 10.8 Hz, 1H), 5.74 (d,  $J = 17.5$  Hz, 1H), 5.30 (d,  $J = 11.0$  Hz, 1H).



1-Fluoro-4-vinylbenzene (**2n**). Colorless liquid. (92 mg from **1n**, isolated yield 75%). HPLC yield 92% (using 1-fluoro-4-vinylbenzene (**2n**) ( $t_R = 4.207$  min,  $\lambda_{max} = 264.2$  nm, MeOH/H<sub>2</sub>O = 80: 20 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.42-7.39 (m, 2H), 7.05 (t,  $J = 8.5$  Hz, 2H), 6.72 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.70 (d,  $J = 17.5$  Hz, 1H), 5.26 (d,  $J = 10.8$  Hz, 1H).

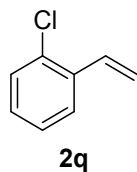


1-Fluoro-3-vinylbenzene (**2o**). Colorless liquid. (85 mg from **1o**, isolated yield 70%). HPLC yield 89% (using 1-fluoro-3-vinylbenzene (**2o**) ( $t_R = 3.192$  min,  $\lambda_{max} = 221.6$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard.<sup>15</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.30-7.25 (m, 1H), 7.17 (d,  $J = 7.7$  Hz, 1H), 7.13 (d,  $J = 10.2$  Hz, 1H), 6.96 (td,  $J = 8.5$  Hz, 1.9 Hz, 1H), 6.69 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.76 (d,  $J = 17.5$  Hz, 1H), 5.31 (d,  $J = 11.0$  Hz, 1H).

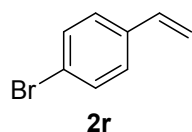


1-Chloro-4-vinylbenzene (**2p**). Colorless liquid. (128 mg from **1p**, isolated yield 92%). The NMR data is identical to that reported in literature.<sup>10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.35 (d,  $J = 8.6$  Hz, 2H), 7.30 (d,  $J = 8.7$  Hz, 2H), 6.68 (dd,  $J = 17.6$  Hz, 10.8 Hz, 1H), 5.74 (d,  $J = 17.5$  Hz, 1H), 5.28 (d,  $J = 10.8$  Hz, 1H).

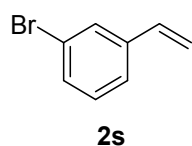




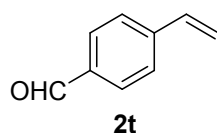
1-Chloro-2-vinylbenzene (**2q**). Colorless liquid. (112 mg from **1q**, isolated yield 81%). HPLC yield 90% (1-chloro-2-vinylbenzene (**2q**) ( $t_R = 3.891$  min,  $\lambda_{max} = 225.2$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>15</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz)  $\delta$  7.71 (dd,  $J = 7.6$  Hz, 1.8 Hz, 1H), 7.44 (dd,  $J = 7.8$  Hz, 1.5 Hz, 1H), 7.35-7.28 (m, 2H), 7.02 (dd,  $J = 17.5$  Hz, 11.1 Hz, 1H), 5.88 (d,  $J = 17.4$  Hz, 1H), 5.44 (d,  $J = 11.1$  Hz, 1H).



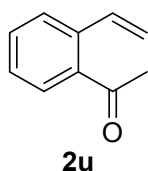
1-Bromo-4-vinylbenzene (**2r**). Colorless liquid. (146 mg from **1r**, isolated yield 80%). HPLC yield 91% (using 1-bromo-4-vinylbenzene (**2r**) ( $t_R = 3.445$  min,  $\lambda_{max} = 253.5$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>16</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.46 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 8.6$  Hz, 2H), 6.67 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.75 (d,  $J = 17.7$  Hz, 1H), 5.29 (d,  $J = 11.0$  Hz, 1H).



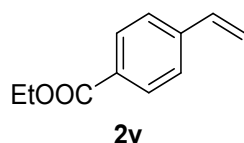
Bromo-3-vinylbenzene(**2s**). Colorless liquid. (148 mg from **1s**, isolated yield 81%). HPLC yield 92% (using bromo-3-vinylbenzene (**2s**) ( $t_R = 3.553$  min,  $\lambda_{max} = 212.2$  nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>13</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.58 (s, 1H), 7.40 (d,  $J = 7.9$  Hz, 1H), 7.33 (d,  $J = 7.8$  Hz, 1H), 7.20 (t,  $J = 7.8$  Hz, 1H), 6.66 (dd,  $J = 17.7$  Hz, 11.0 Hz, 1H), 5.77 (d,  $J = 17.6$  Hz, 1H), 5.32 (d,  $J = 10.8$  Hz, 1H).



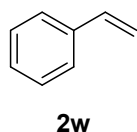
4-Vinylbenzaldehyde (**2t**). Colorless liquid. (106 mg from **1t**, isolated yield 80%). The NMR data is identical to that reported in literature.<sup>17</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  9.99 (s, 1H), 7.84 (d,  $J = 8.4$  Hz, 2H), 7.55 (d,  $J = 8.1$  Hz, 2H), 6.77 (dd,  $J = 17.5$  Hz, 10.8 Hz, 1H), 5.91 (d,  $J = 17.7$  Hz, 1H), 5.44 (d,  $J = 10.8$  Hz, 1H).



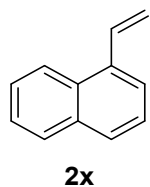
1-(2-Vinylphenyl)ethan-1-one (**2u**). Colorless liquid. (114 mg from **1u**, isolated yield 78%). The NMR data is identical to that reported in literature.<sup>18</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 17.6 Hz, 11.2 Hz, 1H), 5.64 (d, *J* = 17.4 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 2.58 (s, 3H).



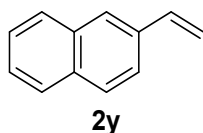
Ethyl 4-vinylbenzoate (**2v**). Colorless liquid. (144 mg from **1v**, isolated yield 82%). The NMR data is identical to that reported in literature.<sup>18</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 17.6 Hz, 10.9 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).



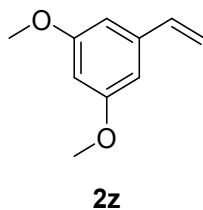
Styrene (**2w**). Colorless liquid. (84 mg from **1w**, isolated yield 81%). HPLC yield 94% (using Styrene (**2w**) (*t<sub>R</sub>* = 2.957 min, λ<sub>max</sub> = 246.4 nm, MeOH/H<sub>2</sub>O = 90: 10 (v / v)) as the external standard. The NMR data is identical to that reported in literature.<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.84 (dd, *J* = 17.6 Hz, 10.9 Hz, 1H), 5.87 (d, *J* = 17.7 Hz, 1H), 5.36 (d, *J* = 11.0 Hz, 1H).



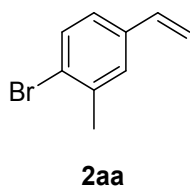
1-Vinylnaphthalene (**2x**). Colorless liquid. (123 mg from **1x**, isolated yield 80%). The NMR data is identical to that reported in literature.<sup>11</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.89-7.87 (m, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.56-7.47 (m, 4H), 5.83 (dd, *J* = 17.4 Hz, 1.6 Hz, 1H), 5.51 (dd, *J* = 10.8 Hz, 1.5 Hz, 1H).



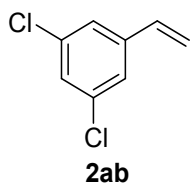
2-Vinylnaphthalene (**2y**). White solid. (120 mg from **1y**, isolated yield 78%). The NMR data is identical to that reported in literature.<sup>16</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.85-7.82 (m, 3H), 7.79 (s, 1H), 7.67 (d,  $J = 8.6$  Hz, 1H), 7.51-7.46 (m, 2H), 6.92 (dd,  $J = 17.7$  Hz, 11.0 Hz, 1H), 5.91 (d,  $J = 17.5$  Hz, 1H), 5.38 (d,  $J = 10.8$  Hz, 1H).



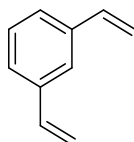
1,3-Dimethoxy-5-vinylbenzene (**2z**). Colorless liquid. (140 mg from **1z**, isolated yield 85%). The NMR data is identical to that reported in literature.<sup>19</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  6.66 (dd,  $J = 17.6$  Hz, 10.9 Hz, 1H), 6.58 (d,  $J = 2.2$  Hz, 2H), 6.40 (t,  $J = 2.0$  Hz, 1H), 5.74 (d,  $J = 17.5$  Hz, 1H), 5.26 (d,  $J = 10.9$  Hz, 1H), 3.81 (s, 6H).



1-Bromo-2-methyl-4-vinylbenzene (**2aa**). Colorless liquid. (162 mg from **1aa**, isolated yield 82%). The NMR data is identical to that reported in literature.<sup>20</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.48 (d,  $J = 8.3$  Hz, 1H), 7.10 (dd,  $J = 8.3$  Hz, 2.0 Hz, 1H), 6.64 (dd,  $J = 17.6$  Hz, 10.8 Hz, 1H), 5.74 (d,  $J = 17.7$  Hz, 1H), 5.27 (d,  $J = 10.8$  Hz, 1H), 2.40 (s, 3H).

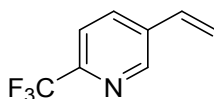


1,3-Dichloro-5-vinylbenzene (**2ab**). Colorless liquid. (151 mg from **1ab**, isolated yield 87%). The NMR data is identical to that reported in literature.<sup>21</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.26 (d,  $J = 1.6$  Hz, 2H), 7.24 (t,  $J = 1.7$  Hz, 1H), 6.59 (dd,  $J = 17.6$  Hz, 10.9 Hz, 1H), 5.77 (d,  $J = 17.5$  Hz, 1H), 5.37 (d,  $J = 10.8$  Hz, 1H).



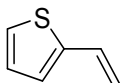
**2ac**

1,3-Divinylbenzene (**2ac**). Colorless liquid. (107 mg from **1ac**, isolated yield 82%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.47 (s, 1H), 7.37-7.31 (m, 3H), 6.76 (dd,  $J = 17.7$  Hz, 11.0 Hz, 2H), 5.81 (d,  $J = 17.5$  Hz, 2H), 5.30 (d,  $J = 11.0$  Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  138.0, 136.9, 128.8, 125.8, 124.4, 114.2. ESI-MS HRMS calculated for  $\text{C}_{10}\text{H}_{11}$   $[\text{M}+\text{H}]^+$  131.0855, found: 131.0849.



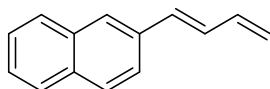
**2ad**

2-(Trifluoromethyl)-5-vinylpyridine (**2ad**). Colorless liquid. (164 mg from **1ad**, isolated yield 95%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.71 (s, 1H), 7.87 (dd,  $J = 8.1$  Hz, 1.2 Hz, 1H), 7.64 (d,  $J = 8.2$  Hz, 1H), 6.75 (dd,  $J = 17.7$  Hz, 11.0 Hz, 1H), 5.94 (d,  $J = 17.5$  Hz, 1H), 5.53 (d,  $J = 11.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  148.3, 147.0 (q,  $J = 35.4$  Hz), 136.0, 134.0, 132.3, 121.7 (q,  $J = 273.4$  Hz), 120.4 (q,  $J = 2.7$  Hz), 119.0. ESI-MS HRMS calculated for  $\text{C}_8\text{H}_7\text{F}_3\text{N}$   $[\text{M}+\text{H}]^+$  174.0525, found: 174.0521.



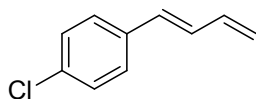
**2ae**

2-Vinylthiophene (**2ae**) Colorless liquid. (91 mg from **1ae**, isolated yield 83%). The NMR data is identical to that reported in literature.<sup>22</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.17 (d,  $J = 4.6$  Hz, 1H), 6.98-6.96 (m, 2H), 6.82 (dd,  $J = 17.2$  Hz, 10.8 Hz, 1H), 5.58 (d,  $J = 17.4$  Hz, 1H), 5.14 (d,  $J = 10.8$  Hz, 1H).



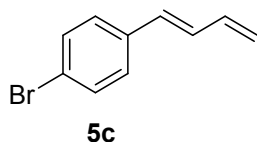
**5a**

(*E*)-2-(buta-1,3-dien-1-yl)naphthalene (**5a**). White solid. (141 mg from **4a**, isolated yield 78%). The NMR data is identical to that reported in literature.<sup>23</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.82-7.79 (m, 3H), 7.77 (s, 1H), 7.64 (dd,  $J = 8.5$  Hz, 1.0 Hz, 1H), 7.49-7.44 (m, 2H), 6.94 (dd,  $J = 15.5$  Hz, 10.4 Hz, 1H), 6.75 (d,  $J = 15.7$  Hz, 1H), 6.63-6.55 (m, 1H), 5.41 (d,  $J = 17.0$  Hz, 1H), 5.24 (d,  $J = 10.1$  Hz, 1H).

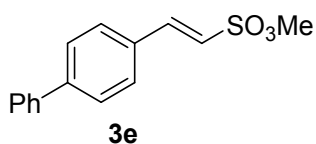


**5b**

(*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (**5b**). Yellow solid. (119 mg from **4b**, isolated yield 72%). The NMR data is identical to that reported in literature.<sup>23</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.76 (dd, *J* = 15.6 Hz, 10.7 Hz, 1H), 6.53-6.47 (m, 2H), 5.36 (d, *J* = 16.8 Hz, 1H), 5.21 (d, *J* = 9.9 Hz, 1H).



(*E*)-1-bromo-4-(buta-1,3-dien-1-yl)benzene (**5c**). White solid. (171 mg from **4c**, isolated yield 82%). The NMR data is identical to that reported in literature.<sup>23</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.77 (dd, *J* = 15.5 Hz, 10.5 Hz, 1H), 6.53-6.46 (m, 2H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H).



Methyl (*E*)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonate (**3e**). white solid (1.0 g from **1a**, isolated yield 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.69-7.65 (m, 3H), 7.63-7.59 (m, 4H), 7.50-7.47 (m, 2H), 7.43-7.39 (m, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 3.88 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) δ 145.1, 144.5, 139.8, 130.9, 129.2, 129.1, 128.4, 128.0, 127.2, 120.0, 56.3. ESI-MS HRMS calculated for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 275.0736, found: 275.0735.

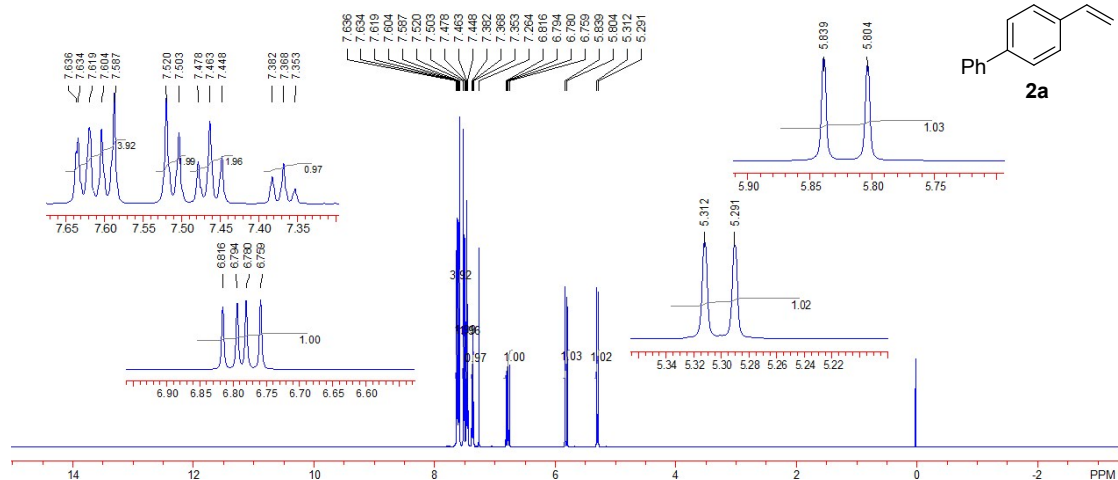
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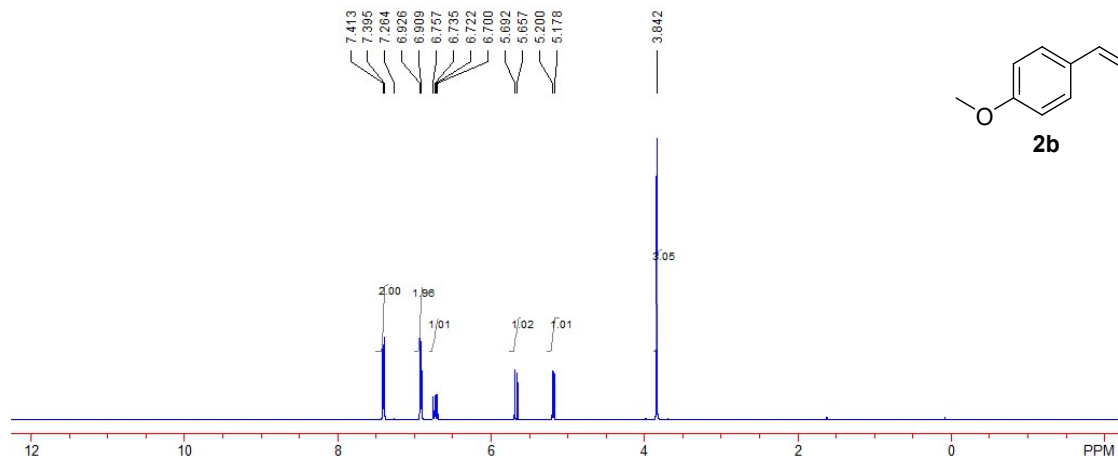
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## 6. NMR spectra.

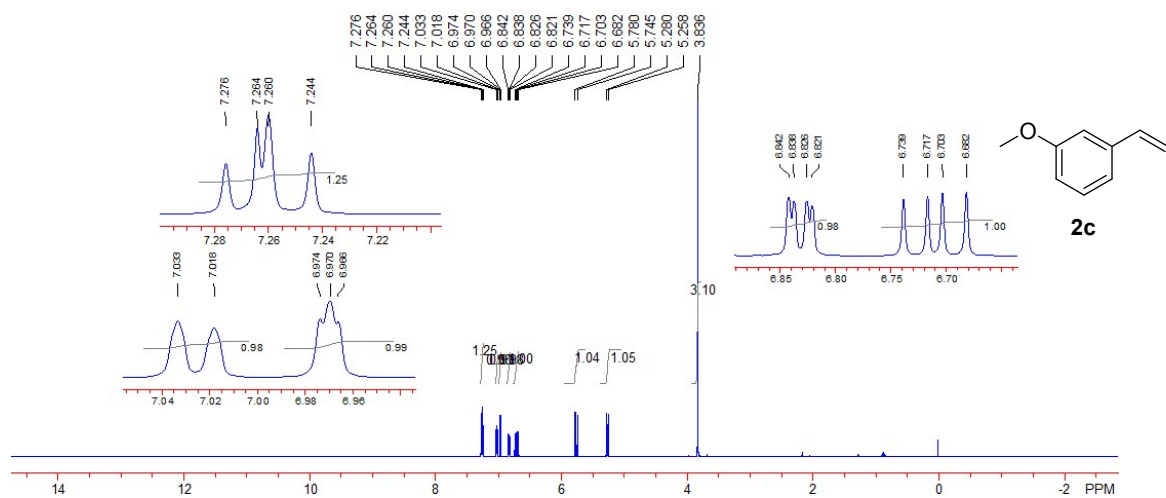
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### 2b, <sup>1</sup>H NMR, 500 MHz, CDCl<sub>3</sub>

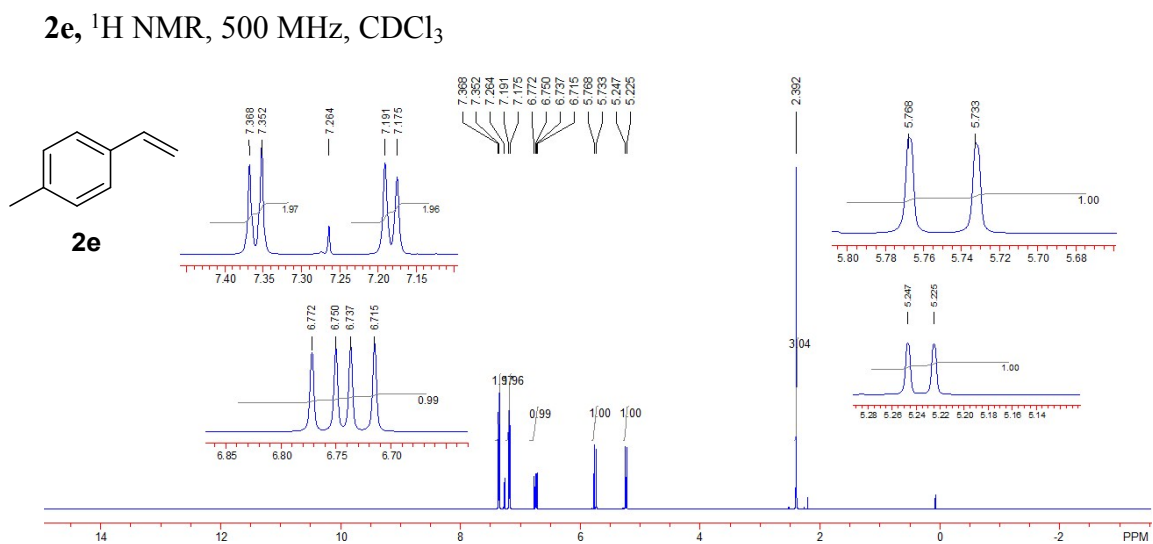
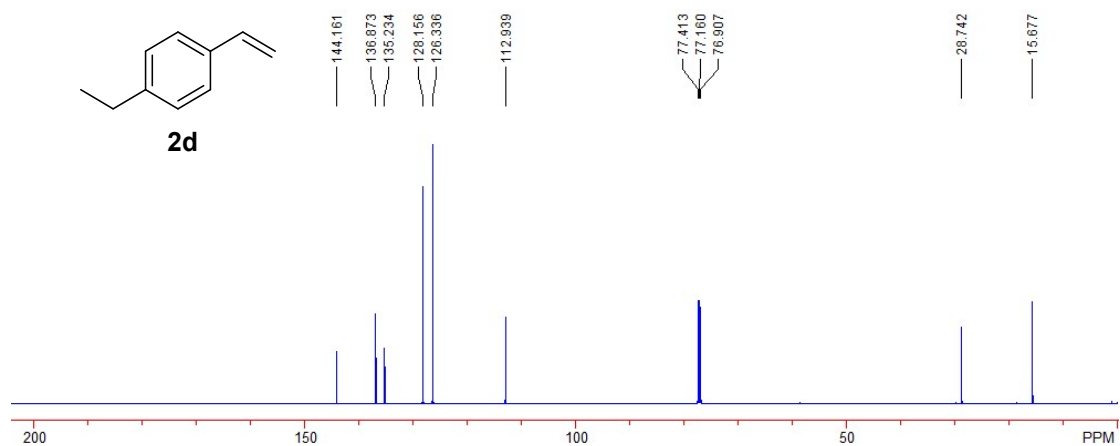
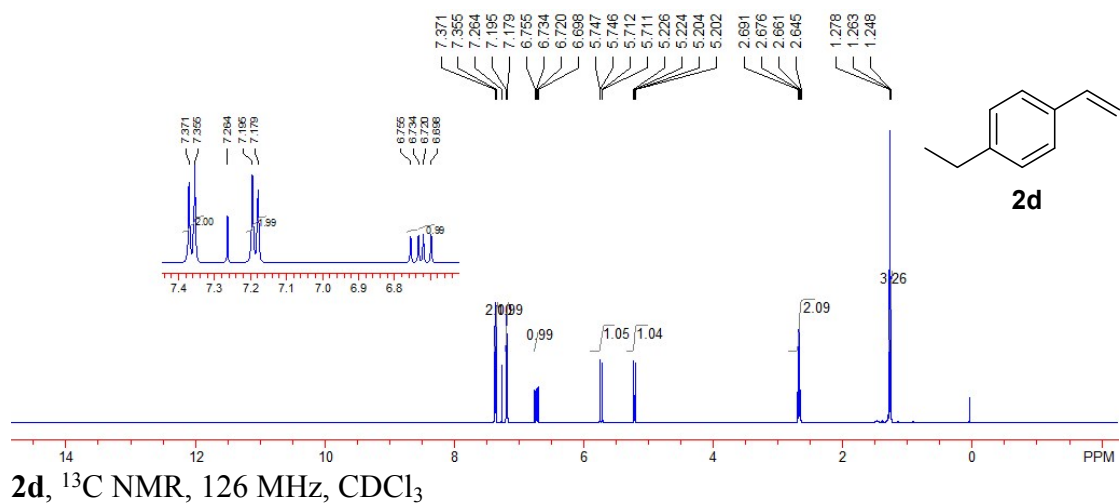


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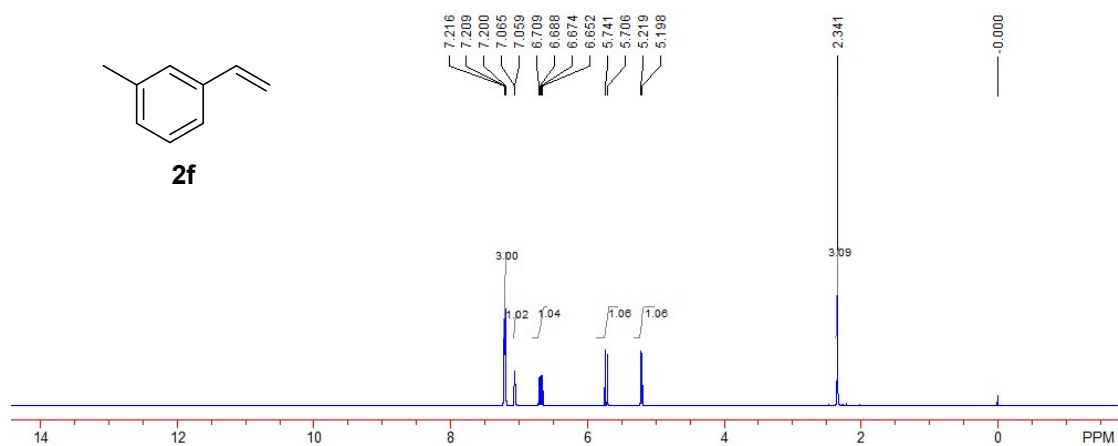


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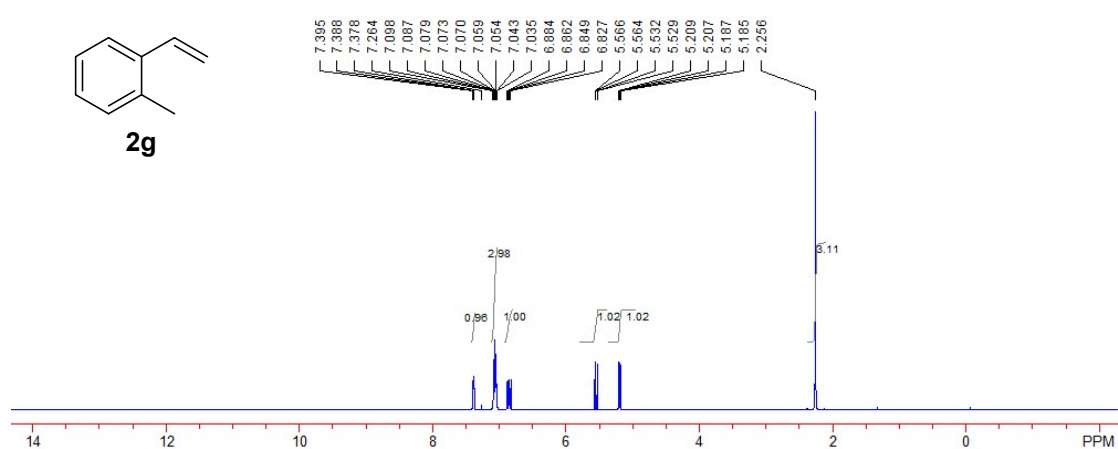




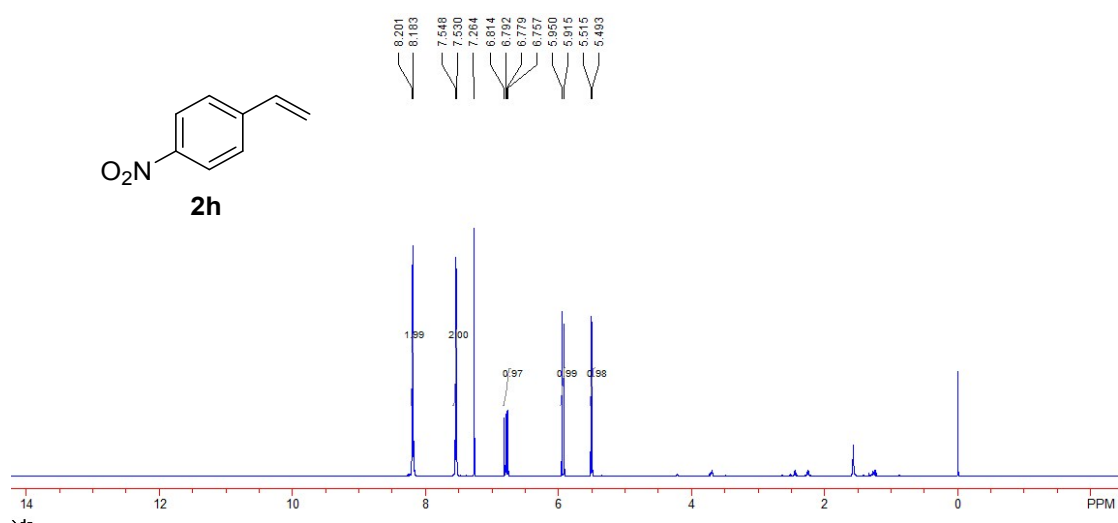
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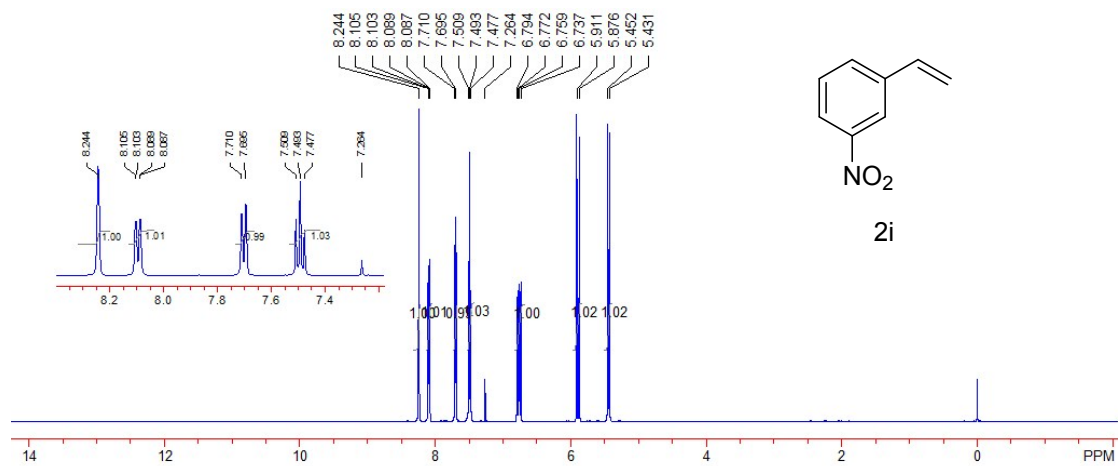
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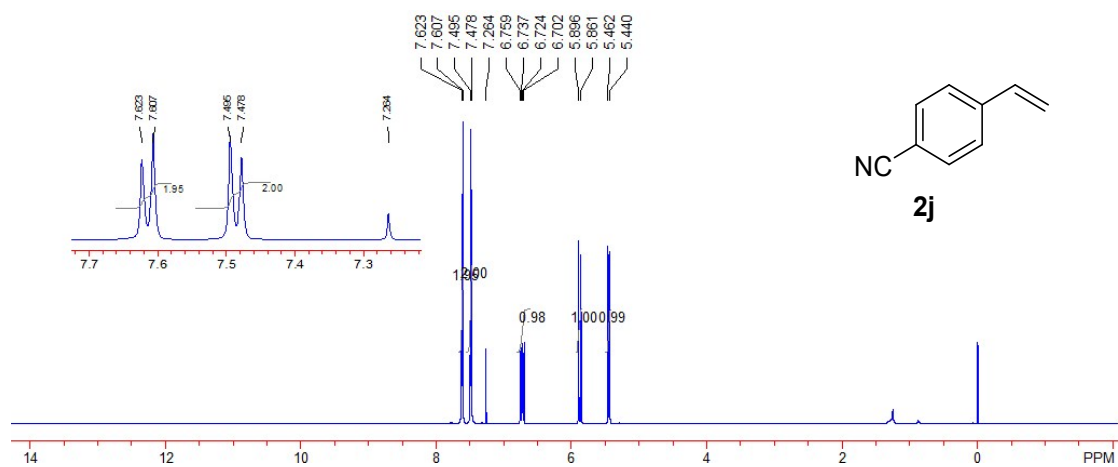
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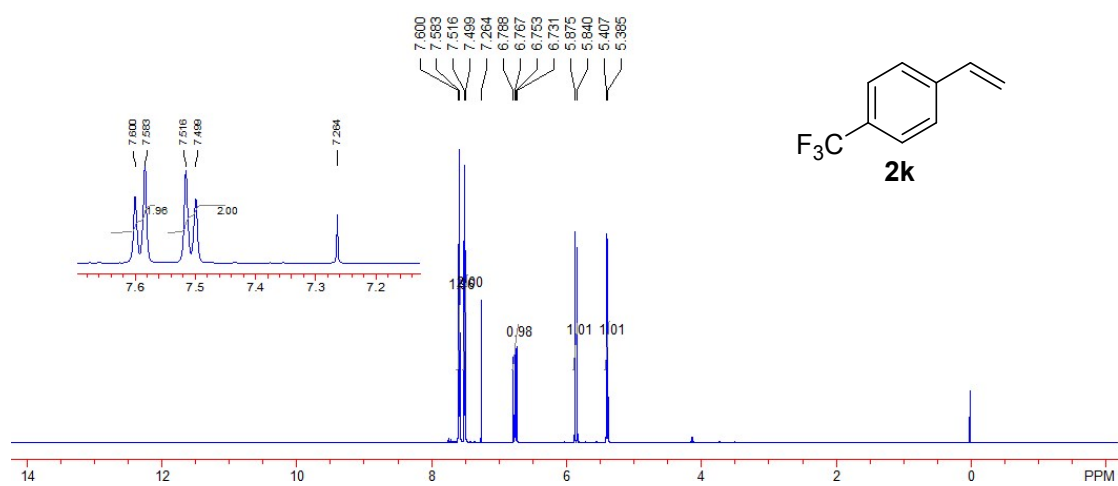
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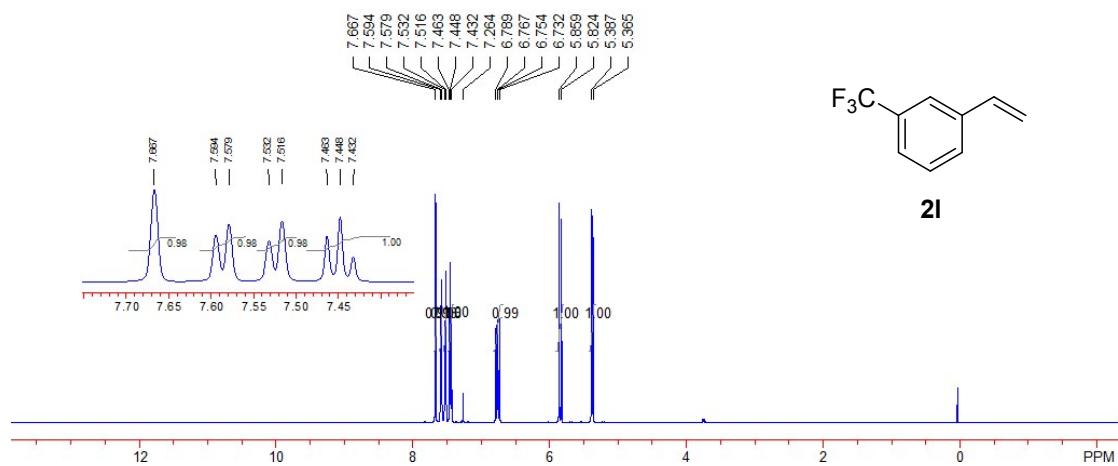
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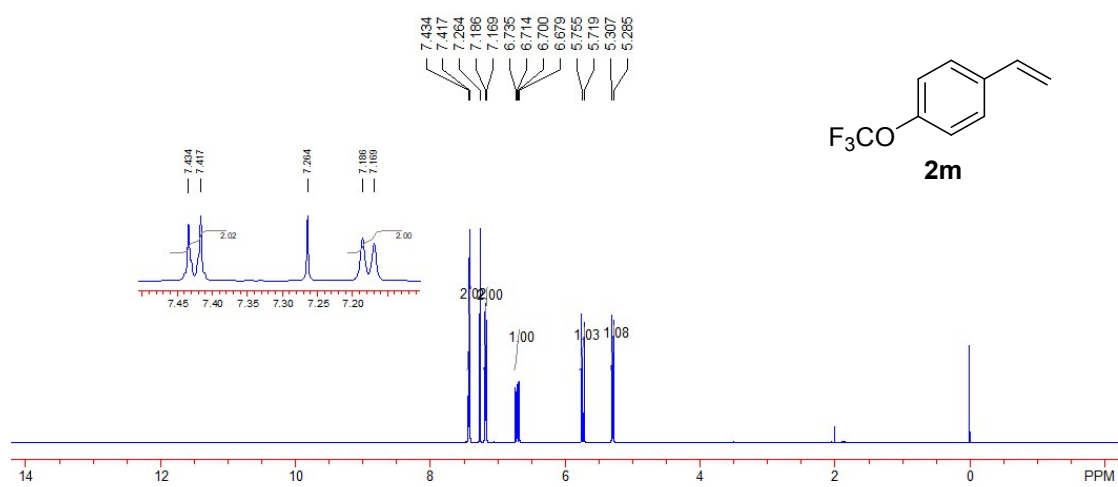
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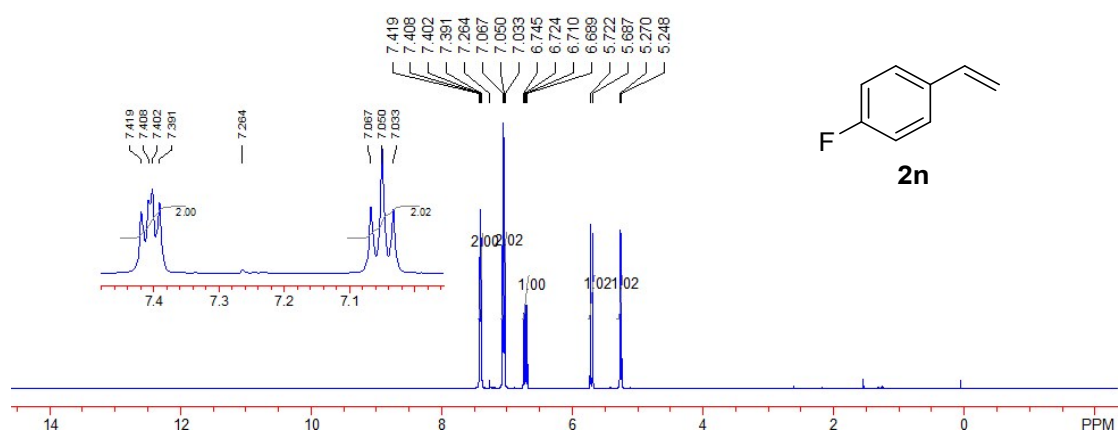
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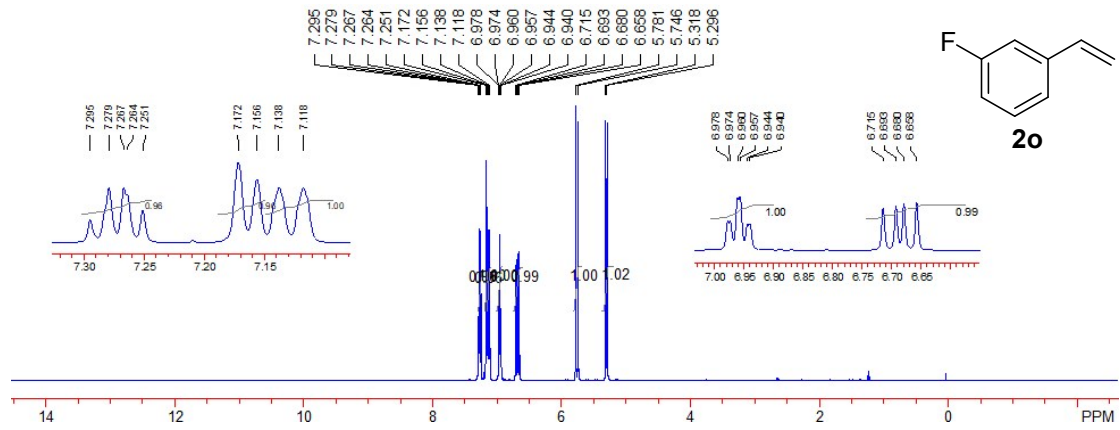
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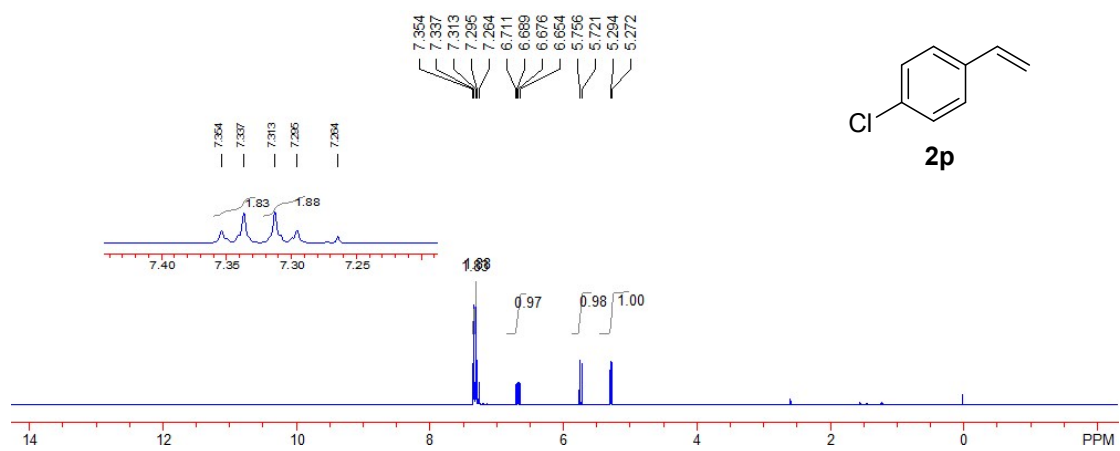
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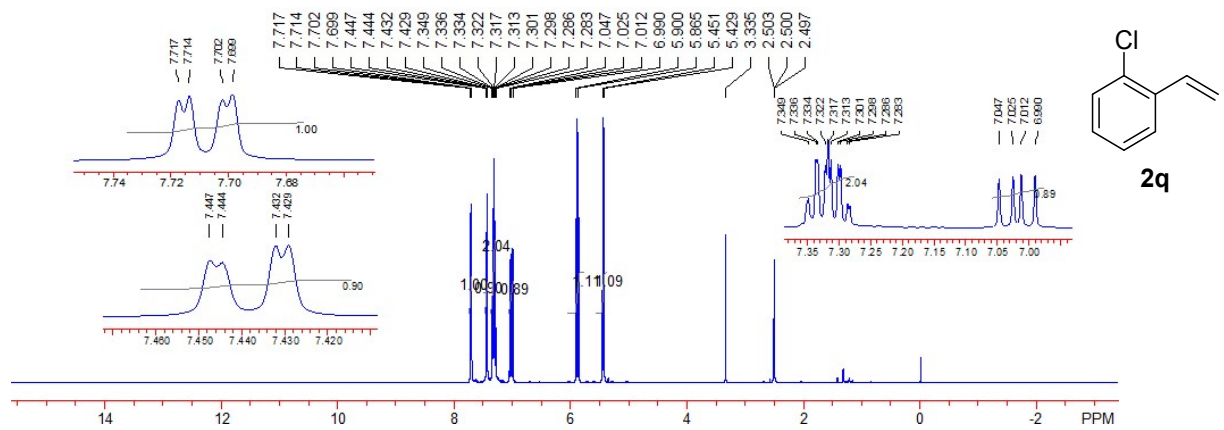
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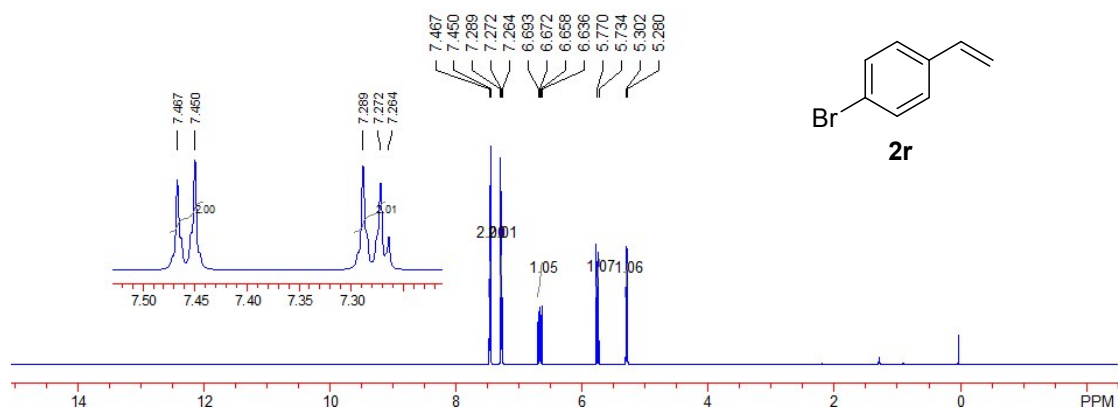
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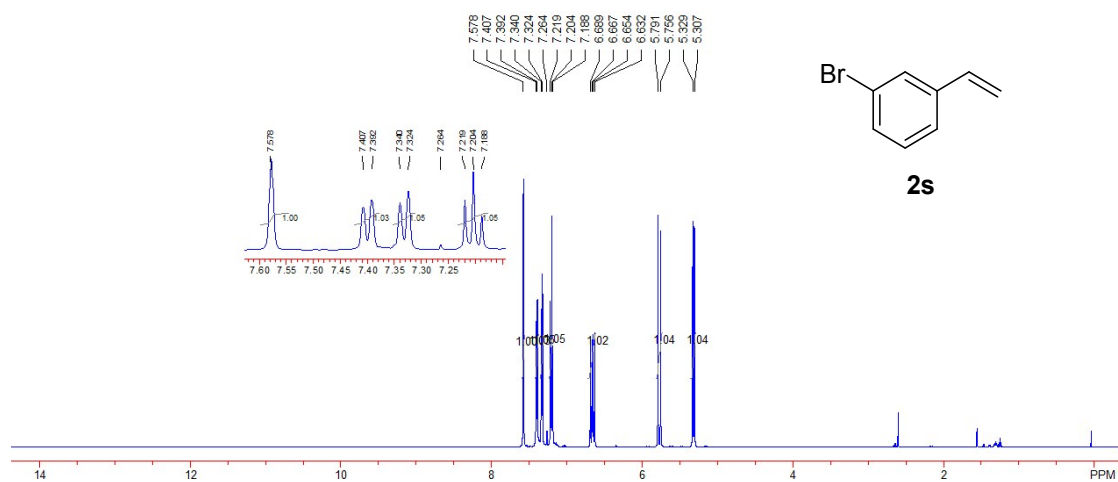
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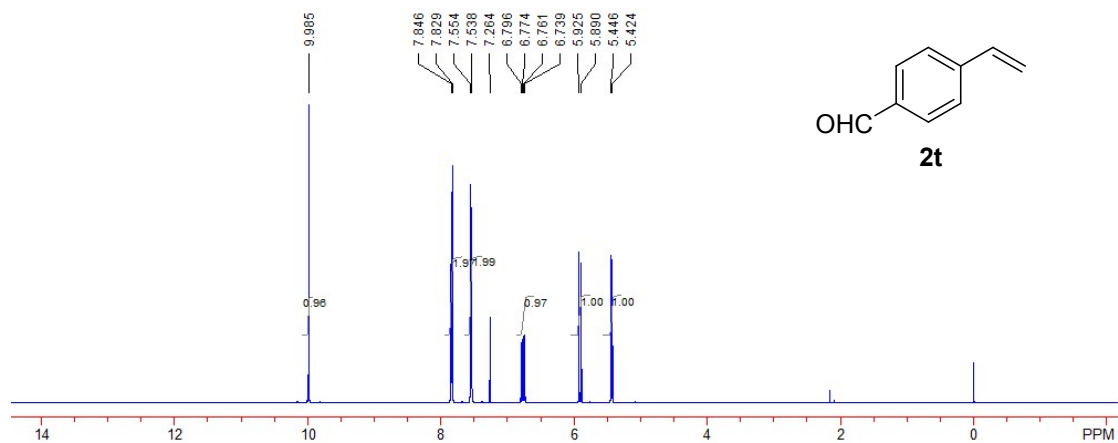
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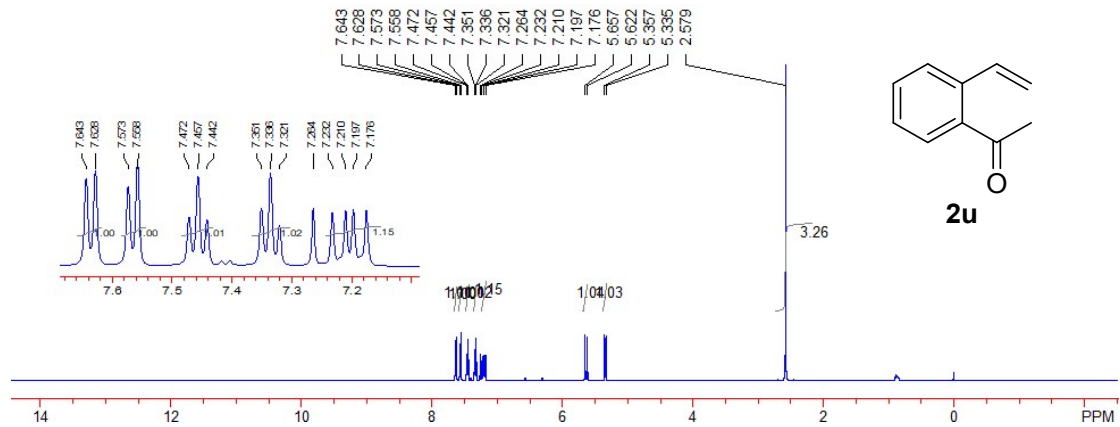
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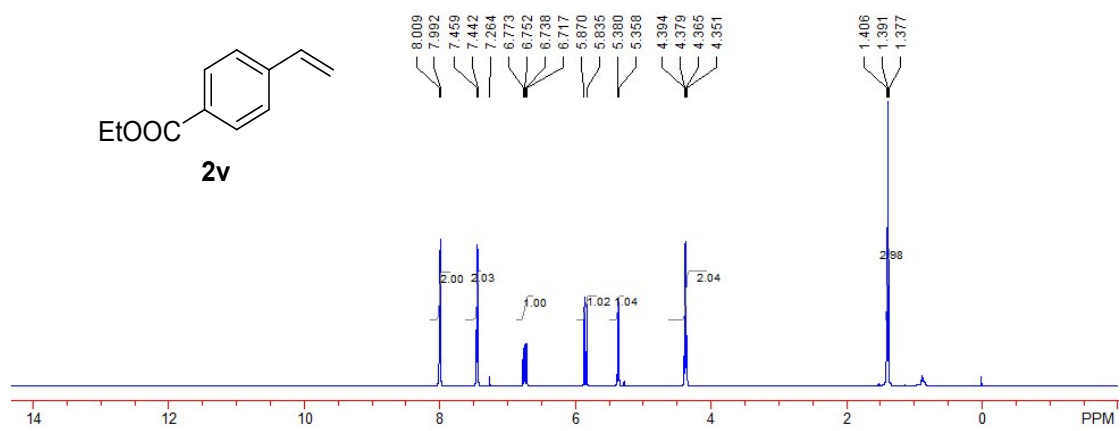
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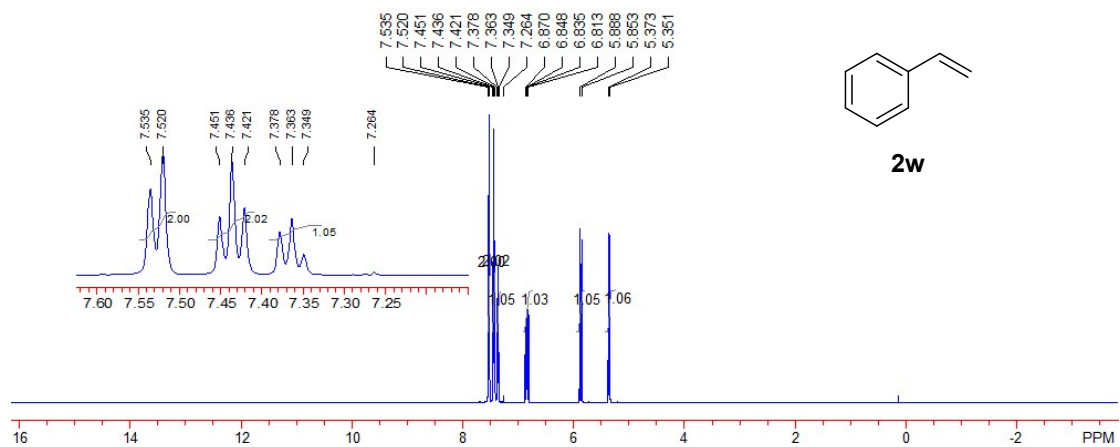
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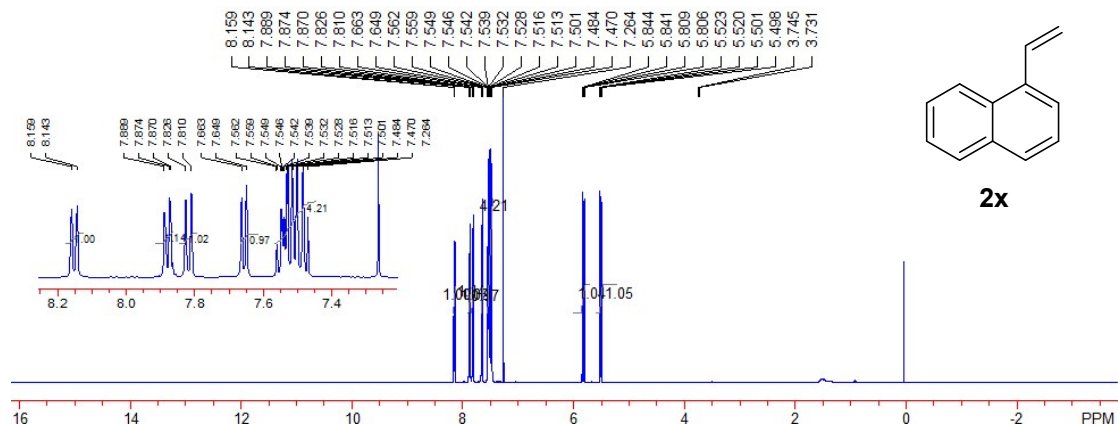
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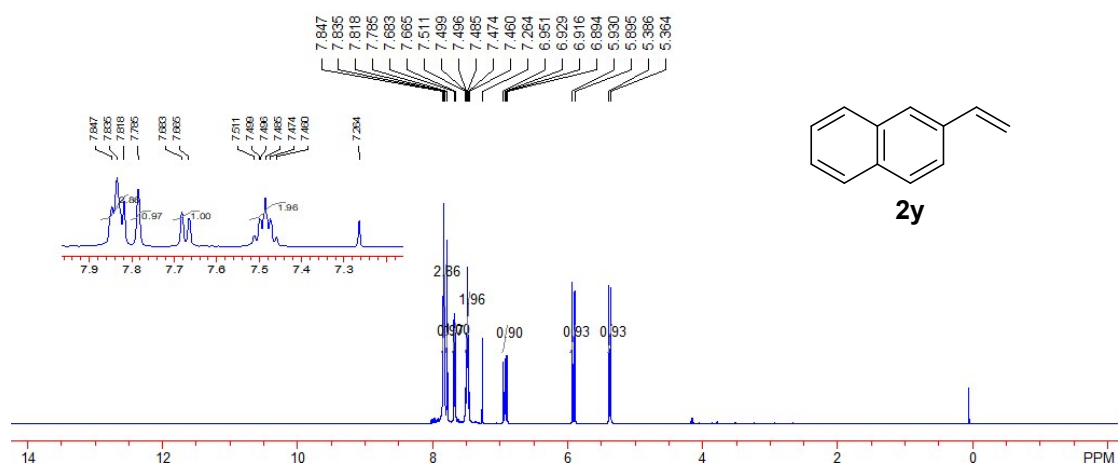
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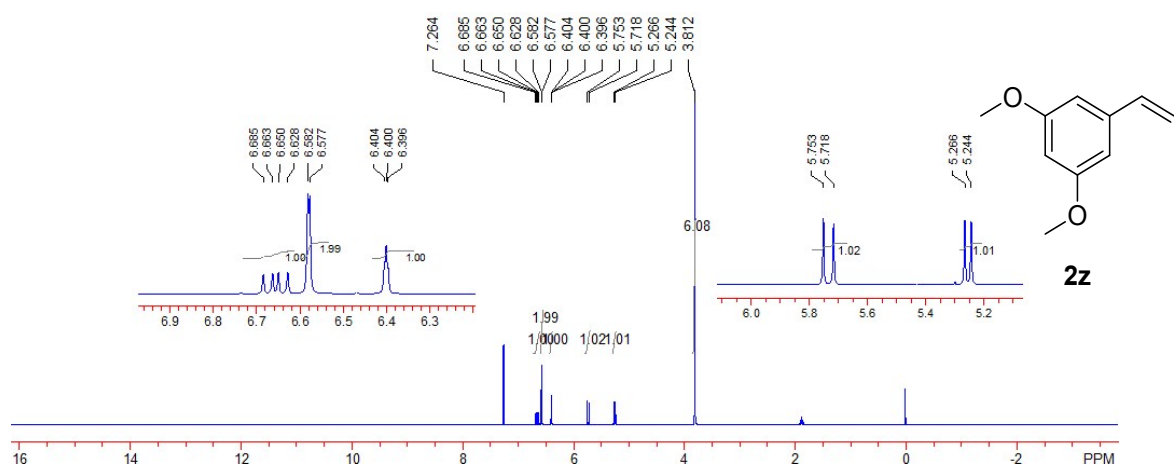
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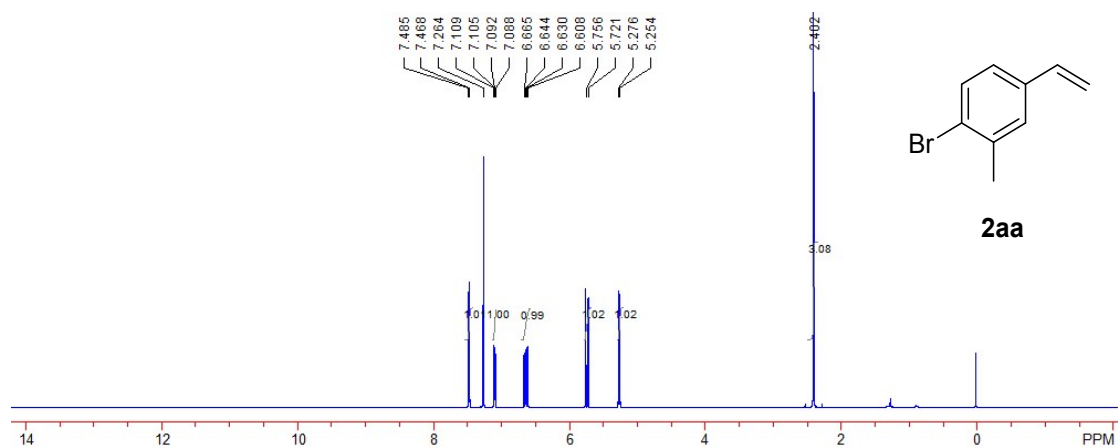


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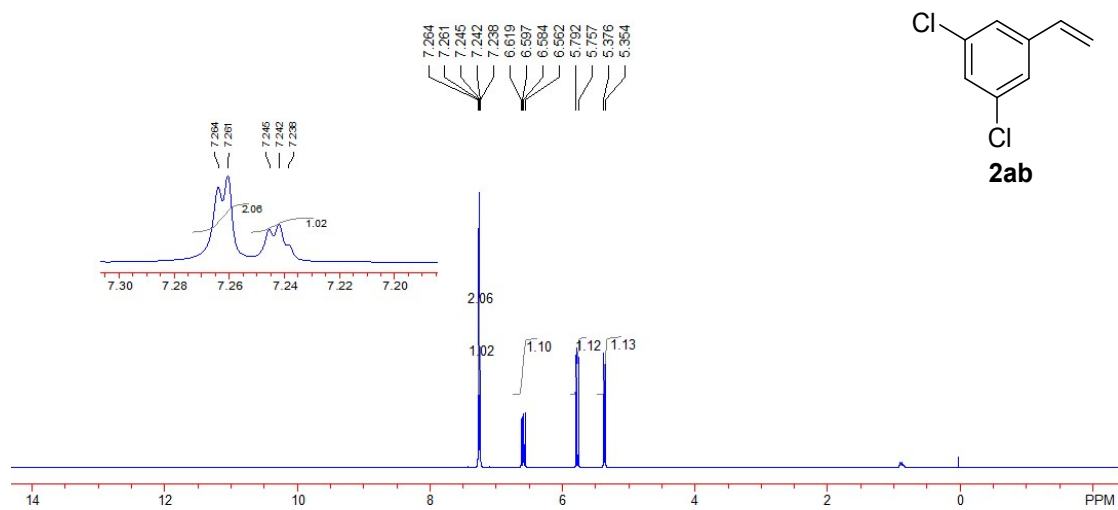


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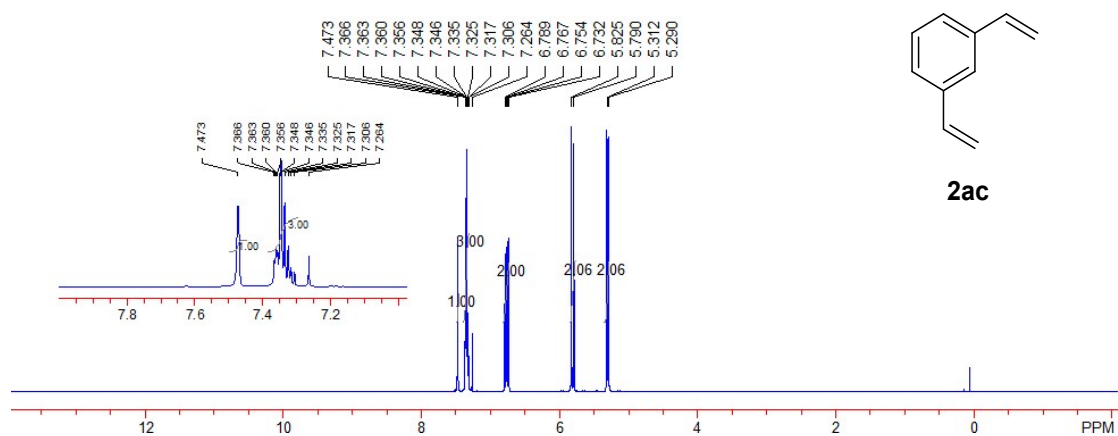




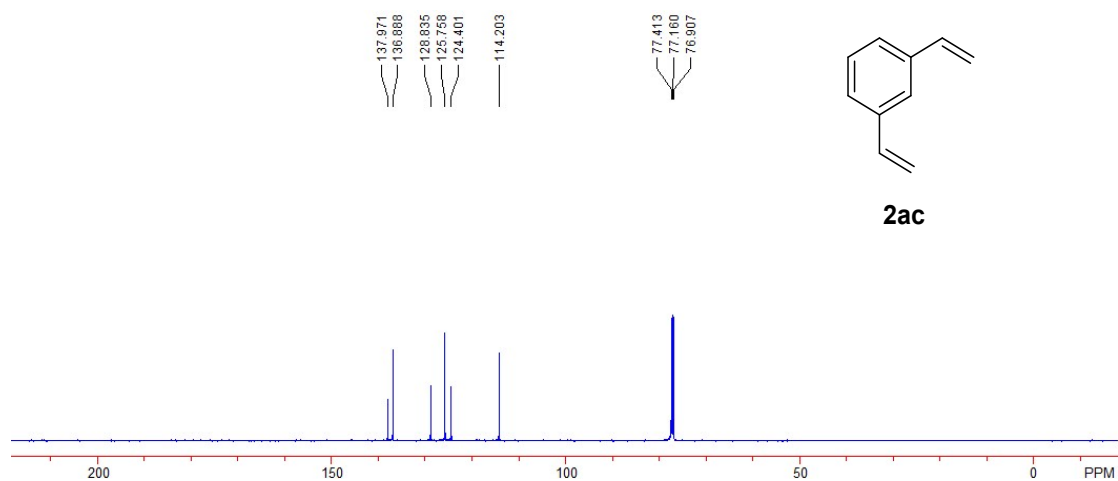
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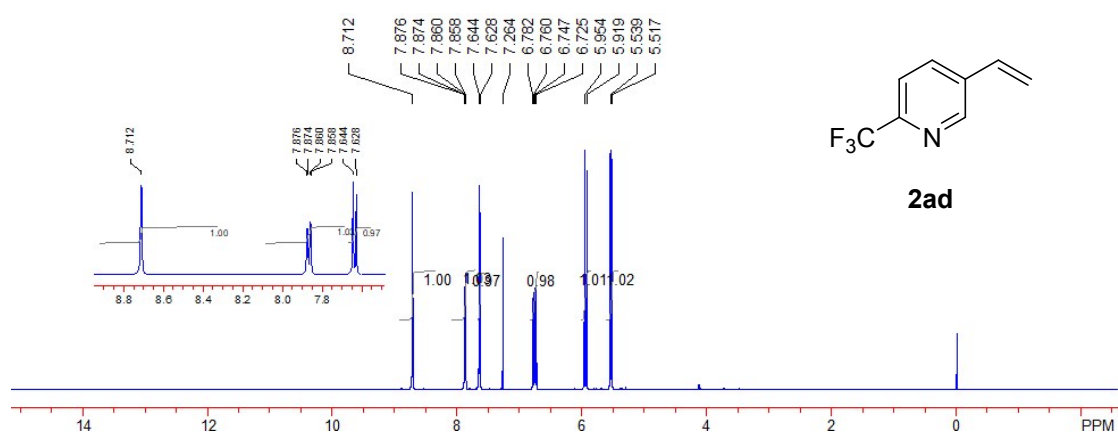
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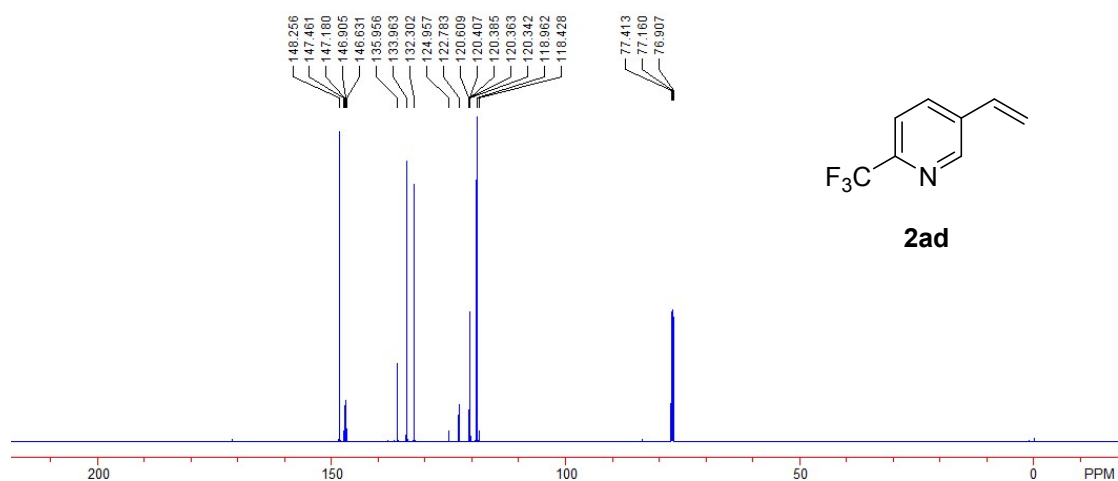
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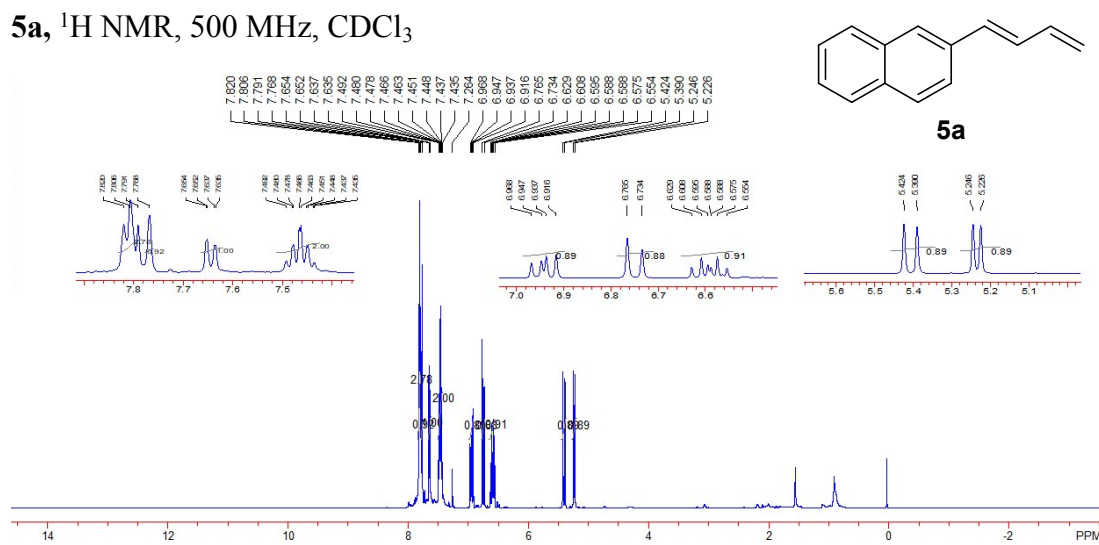
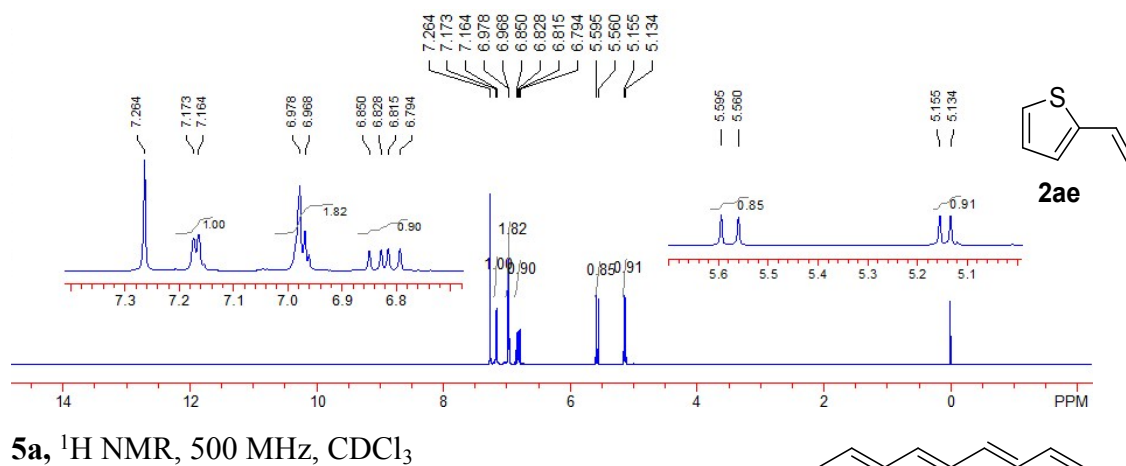
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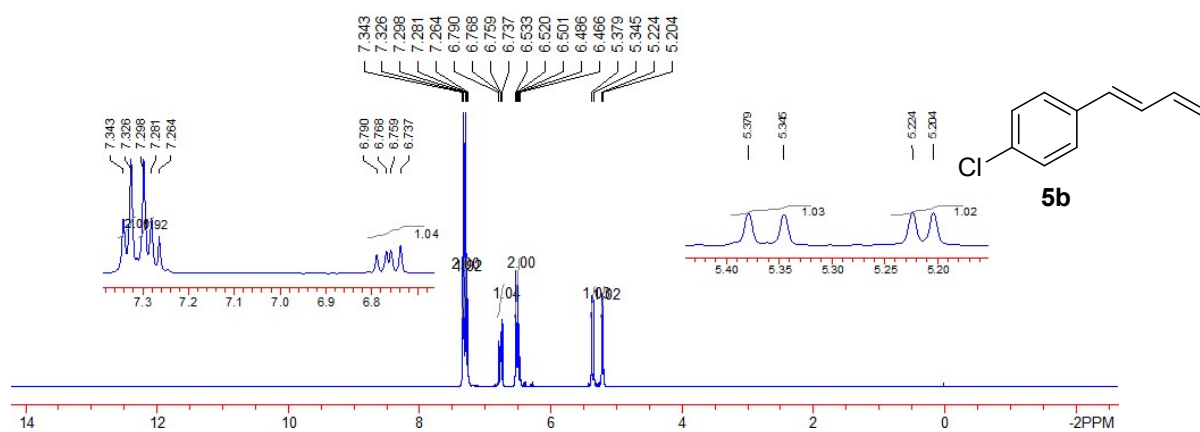
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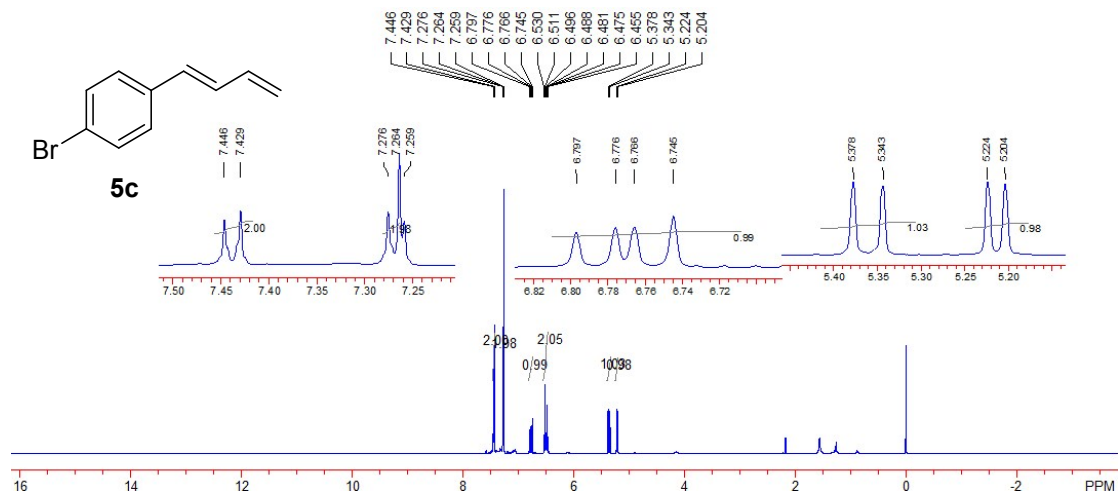
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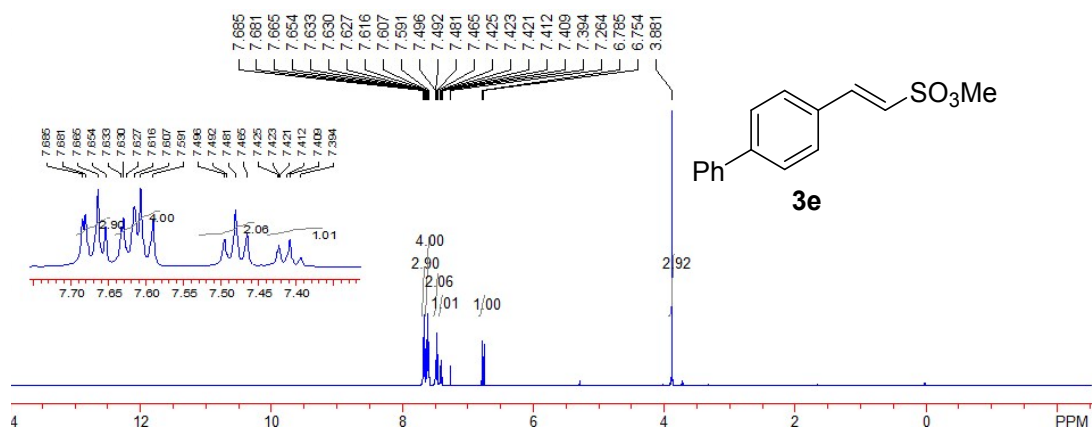
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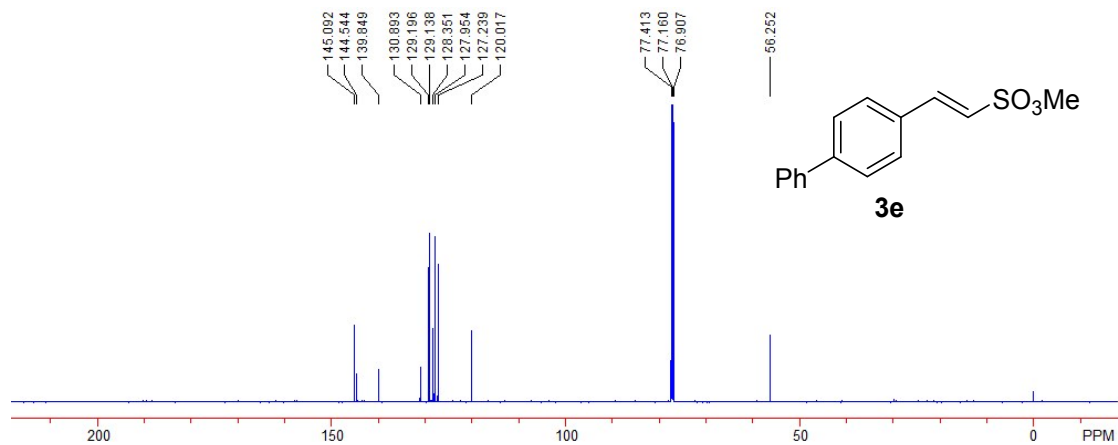
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**3e**, <sup>13</sup>C NMR, 126 MHz, CDCl<sub>3</sub>



**2a'+2a''**, <sup>1</sup>H NMR, 500 MHz, CDCl<sub>3</sub>

