

## Palladium/Norbornene-Catalyzed Decarbonylative Difunctionalization of Thioesters

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## Supporting Information

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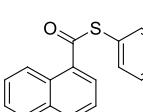
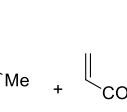
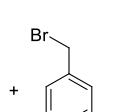
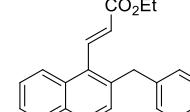
## 1. General information

All commercial reagents were purchased from TCI, j&k, STREM, Sigma-Aldrich, Adamas-beta, 9-Ding chemistry, and Energy Chemical of the highest purity grade. They were used without further purification unless specified. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under (140 °C) oven for two hours prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE III 400 and Bruker AVANCE III 500 instruments. The peaks were internally referenced to TMS (0.00 ppm). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. EI-double focus magnetic-sector high resolution MS (EI-DFS-HRMS) was recorded on a DFS-Thermostischer instrument employing an ultra-high precision toroidal electrostatic analyzer (ESA) and a carefully refined magnetic analyzer at the Center for Mass Spectrometry, Shanghai Institute of Material Medica. ESI with TOF analyzer was carried out at the Center for Mass Spectrometry, Shanghai Institute of Material Medica.

## 2. Optimization reaction conditions

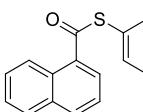
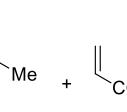
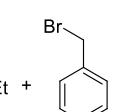
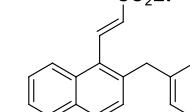
### 2.1 Optimization of the ortho-benzylation/*ipso*-Heck reaction conditions

**Table S1.** Screening of the solvents<sup>a</sup>

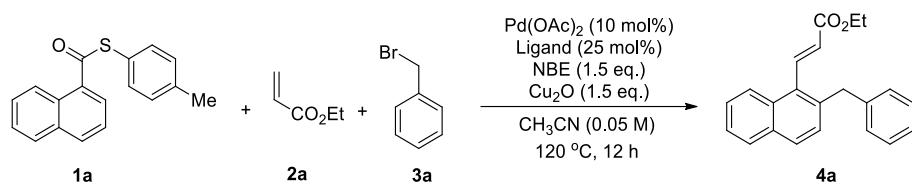
 1a	 2a	 3a	Pd(OAc) <sub>2</sub> (10 mol%) TFP (25 mol%) NBE (1.5 eq.) Cu <sub>2</sub> O (1.5 eq.) Na <sub>2</sub> CO <sub>3</sub> (2.0 eq.) Solvent (0.05 M) 120 °C, 12 h	 4a
Entry			Solvent	Yield (%)
1			NMP	<5
2			MeCN	61
3			THF	N.D.
4			Dioxane	<5
5			DMF	23

<sup>a</sup>Yields was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S2.** Screening of the bases<sup>a</sup>

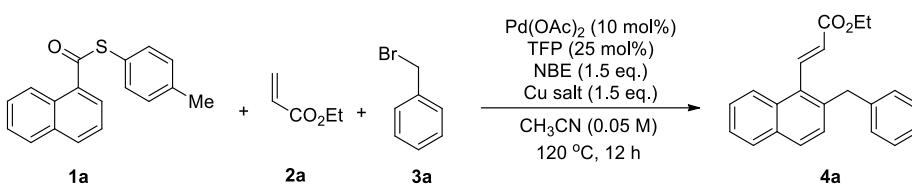
 1a	 2a	 3a	Pd(OAc) <sub>2</sub> (10 mol%) TFP (25 mol%) NBE (1.5 eq.) Cu <sub>2</sub> O (1.5 eq.) Base (2.0 eq.) CH <sub>3</sub> CN (0.05 M) 120 °C, 12 h	 4a
Entry			Base	Yield (%)
1			K <sub>2</sub> CO <sub>3</sub>	<5
2			Cs <sub>2</sub> CO <sub>3</sub>	trace
3			MeONa	<5
4			Na <sub>2</sub> CO <sub>3</sub>	61
5			PhCOONa	55
6			NaOAc	66
7			KH <sub>2</sub> PO <sub>4</sub>	43
8			—	68

<sup>a</sup>Yields was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S3.** Screening of the ligands<sup>a</sup>

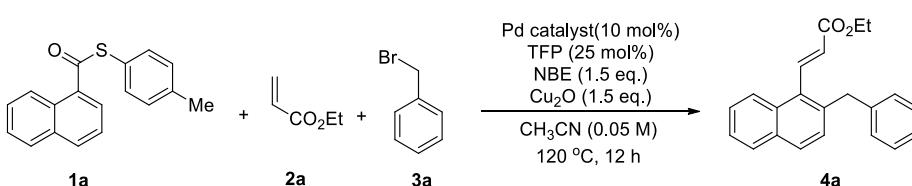
Entry	Ligand	Yield (%)
1	dppf	N.D.
2	DPEPhos	42
3	<i>t</i> -Bu-Xantphos	trace
4	dcype	17
5	(3,5-diMePh) <sub>3</sub> P	15
6	Cy <sub>3</sub> P	16
7	( <i>p</i> -MePh) <sub>3</sub> P	trace
8	sPhos	N.D.
9	( <i>o</i> -MeOPh) <sub>3</sub> P	14
10	<i>t</i> -BuXPhos	<5
11	TFP	68

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S4.** Screening of the Cu salts<sup>a</sup>

Entry	Cu salt	Yield (%)
1	CuTc	28
2	CuBr	15
3	CuI	13
4	CuOAc	44
5	CuCN	N.D.
6	Cu <sub>2</sub> O	68

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S5.** Screening of the Pd catalysts<sup>a</sup>

Entry	Pd catalyst	Yield (%)
1	Pd(TFA) <sub>2</sub>	63
2	PdCl <sub>2</sub>	61
3	Pd <sub>2</sub> (dba) <sub>3</sub>	49
4	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	57
5	PdCl <sub>2</sub> •dppf	41
6	Pd(acac) <sub>2</sub>	46
7	Pd(OAc) <sub>2</sub>	68

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S6.** Screening of the temperatures<sup>a</sup>

			Pd(OAc) <sub>2</sub> (10 mol%) TFP (25 mol%) NBE (1.5 eq.) Cu <sub>2</sub> O (1.5 eq.) CH <sub>3</sub> CN (0.05 M) <i>T</i> °C, 12 h	
Entry			T (°C)	Yield (%)
1			rt	ND
2			60	35
3			80	52
4			100	65
5			120	68
6			130	63

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S7.** Screening of the leaving groups<sup>a</sup>

			Pd(OAc) <sub>2</sub> (10 mol%) TFP (25 mol%) <b>NBE-6</b> (1.5 eq.) Cu <sub>2</sub> O (1.5 eq.) CH <sub>3</sub> CN (0.05 M) 120 °C, 12 h	
Entry			R	Yield (%)
1				45
2				60
3				57

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

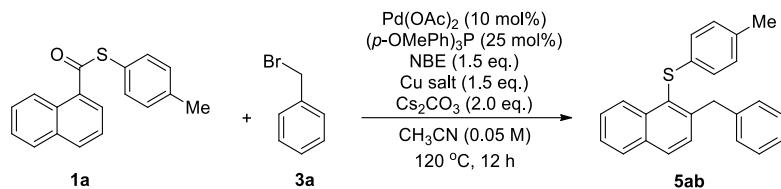
**Table S8.** Screening of the Cu<sub>2</sub>O loading<sup>a</sup>

			Pd(OAc) <sub>2</sub> (10 mol%) TFP (25 mol%) <b>NBE-6</b> (1.5 eq.) Cu <sub>2</sub> O (x eq.) CH <sub>3</sub> CN (0.05 M) 120 °C, 12 h	
Entry			Cu <sub>2</sub> O (x eq.)	Yield (%)
1			0	N.D.
2			0.1	15
3			0.3	25
4			0.5	48
5			1.0	68
6			1.5	85
7			2.0	83

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

## 2.2 Optimization of the ortho-benzylation/ipso-thiolation reaction conditions

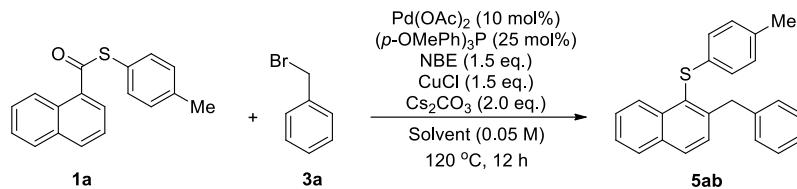
**Table S9.** Screening of the Cu salt<sup>a</sup>



Entry	Cu salt	Yield (%)
1	Cu <sub>2</sub> O	7
2	CuCl	20
3	CuBr	11
4	CuI	trace
5	CuOAc	trace
6	CuTc	7
7	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub>	18

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

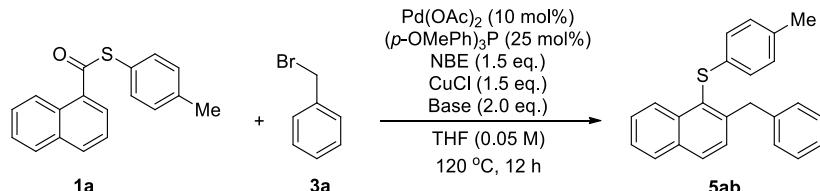
**Table S10.** Screening of the solvents<sup>a</sup>



Entry	Solvent	Yield (%)
1	THF	25
2	dioxane	11
3	DMSO	trace
4	DMF	n.d.
5	toluene	9
6	DCE	18
7	MeCN	20

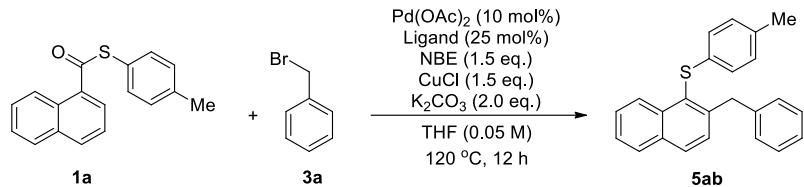
<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S11.** Screening of the bases<sup>a</sup>



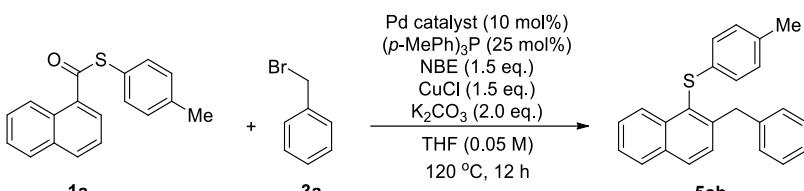
Entry	Base	Yield (%)
1	Li <sub>2</sub> CO <sub>3</sub>	n.d.
2	Na <sub>2</sub> CO <sub>3</sub>	n.d.
3	K <sub>2</sub> CO <sub>3</sub>	27
4	NaHCO <sub>3</sub>	n.d.
5	KHCO <sub>3</sub>	n.d.
6	NaOAc	n.d.
7	NaOMe	12
8	—	n.d.
9	Cs <sub>2</sub> CO <sub>3</sub>	25

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S12.** Screening of the ligand<sup>a</sup>

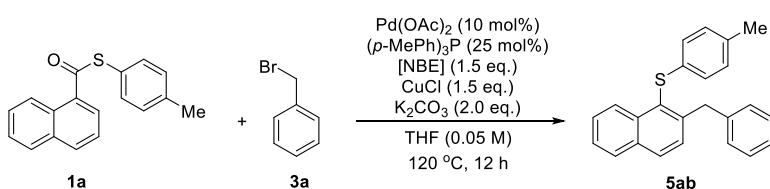
Entry	Ligand	Yield (%)
1	PPh <sub>3</sub>	18
2	( <i>p</i> -MePh) <sub>3</sub> P	41
3	( <i>o</i> -OMePh) <sub>3</sub> P	17
4	PCy <sub>3</sub>	3
5	TFP	5
6	( <i>p</i> -OMePh) <sub>3</sub> P	27

<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S13.** Screening of the Pd catalyst<sup>a</sup>

Entry	Pd catalyst	Yield (%)
1	PdCl <sub>2</sub>	39
2	Pd(acac) <sub>2</sub>	19
3	Pd(OTFA) <sub>2</sub>	20
4	Pd(CH <sub>3</sub> CN) <sub>4</sub> (BF <sub>4</sub> ) <sub>2</sub>	25
5	Pd <sub>2</sub> dba <sub>3</sub>	31
6	Pd(OAc) <sub>2</sub>	41

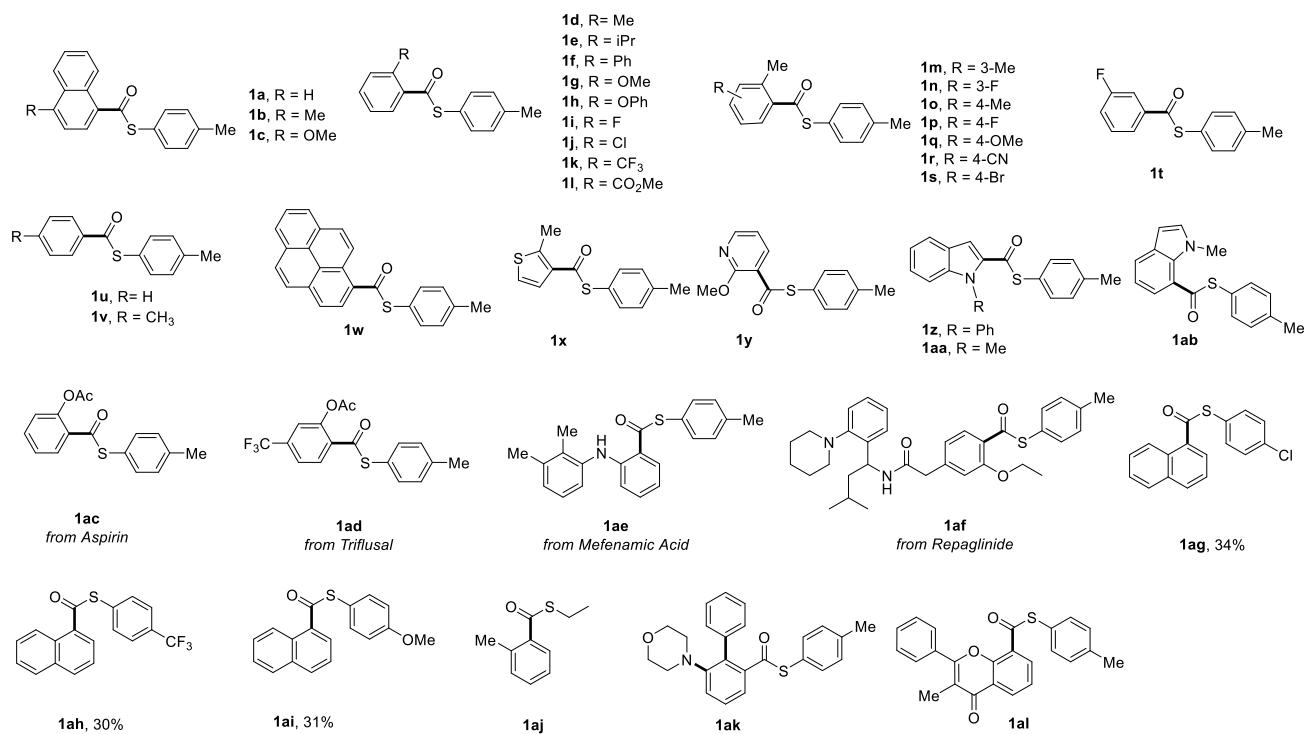
<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard.

**Table S14.** Screening of the substituted NBE<sup>a</sup>

Entry	NBE	Yield (%)
1	NBE-1	38
2	NBE-2	42
3	NBE-3	33
4	NBE-4	36
5	NBE-5	44
6	NBE-6	37
7	NBE-7	12
8	NBE-8	64 (67) <sup>b</sup>
9	NBE-9	53
10	NBE-10	40
11	NBE-11	36
12	NBE-12	12
13	NBE	41

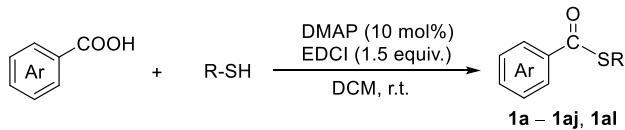
<sup>a</sup>Yield was determined by <sup>1</sup>H NMR analysis of crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal standard. <sup>b</sup>isolated yield.

### 3. General procedures for the preparation of substrates



**Scheme S1.** Aryl thioesters used in this work

#### 3.1 General procedures for the preparation of thioesters

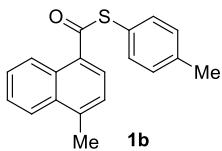


A round-bottom flask, carboxylic acid (10.0 mmol, 1.0 equiv), EDCI (15.0 mmol, 1.5 equiv) and DMAP (1.0 mmol, 0.1 equiv) were dissolved in 50 mL anhydrous DCM. The mixture was stirred for 10 min at room temperature. After that, thiophenol (or thiol) (12.0 mmol, 1.2 equiv) was added to the mixture directly. Then the reaction mixture was stirred at room temperature for another 12 h. The reaction was quenched with  $\text{H}_2\text{O}$  and extracted with DCM (40 mLx2). The organic layer was washed with brine (40 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel to yield the desired product.

#### *S-p-tolyl naphthalene-1-carbothioate (1a)*

Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1a** as a white solid. 63% yield (1.75 g); m.p. 73–74 °C.  
<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (d,  $J = 8.3$  Hz, 1H), 8.22 (d,  $J = 7.1$  Hz, 1H), 8.03 (d,  $J = 8.2$  Hz, 1H), 7.89 (d,  $J = 7.5$  Hz, 1H), 7.62–7.50 (m, 3H), 7.47 (d,  $J = 8.0$  Hz, 2H), 7.31 (d,  $J = 7.9$  Hz, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.89, 140.03, 135.01, 134.85, 133.94, 133.34, 130.31, 129.45, 128.47, 128.20, 128.08, 126.82, 125.46, 124.83, 124.61, 21.57. HRMS (EI-ESA)  $m/z$ : [M]<sup>+</sup> Calcd for  $\text{C}_{18}\text{H}_{14}\text{OS}$  278.0760; Found 278.0763.

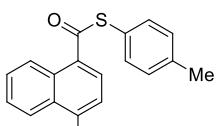
### *S-p-tolyl 4-methylnaphthalene-1-carbothioate (1b)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1b** as a white solid. 67% yield (1.96 g); m.p. 93-94 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.64-8.55 (m, 1H), 8.14 (d, *J* = 7.4 Hz, 1H), 8.05 (dt, *J* = 5.9, 2.7 Hz, 1H), 7.62-7.54 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.76 (s, 3H), 2.42 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.73, 140.58, 139.92, 135.04, 133.25, 133.00, 130.27, 129.53, 128.14, 127.81, 126.67, 126.05, 125.48, 125.05, 124.44, 21.57, 20.31. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>OS 292.0916; Found 292.0908.

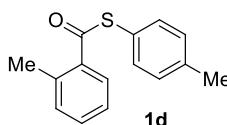
### *S-p-tolyl 4-methoxynaphthalene-1-carbothioate (1c)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1c** as a white solid. 62% yield (1.91 g); m.p. 67-68 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.70 (d, *J* = 8.6 Hz, 1H), 8.36-8.28 (m, 2H), 7.58 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.08 (s, 3H), 2.42 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 191.39, 159.66, 139.78, 135.22, 131.12, 130.89, 130.21, 128.86, 126.78, 126.17, 125.76, 125.48, 125.25, 122.28, 102.40, 56.02, 21.56. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>S 308.0866; Found 308.0848.

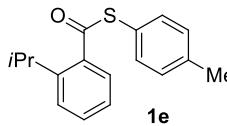
### *S-p-tolyl 2-methylbenzothioate (1d)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1d** as a white solid. 57% yield (1.38 g); m.p. 74-75 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.44-7.38 (m, 3H), 7.32-7.25 (m, 4H), 2.48 (s, 3H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.81, 139.89, 137.53, 136.89, 135.00, 132.08, 131.85, 130.25, 128.75, 125.95, 124.73, 21.53, 20.94. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>OS 242.0760; Found 242.0760.

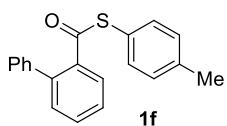
### *S-p-tolyl 2-isopropylbenzothioate (1e)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1e** as a white solid. 67% yield (1.81 g); m.p. 62-63 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44-7.38 (m, 3H), 7.30-7.24 (m, 3H), 3.42 (hept, *J* = 6.8 Hz, 1H), 2.40 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 193.93, 147.32, 139.91, 137.32, 134.79, 131.85, 130.27, 127.97, 126.53, 125.69, 124.92, 29.59, 24.13, 21.52. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>18</sub>OS 270.1073; Found 270.1091.

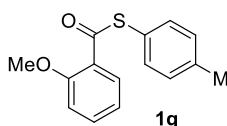
### *S-p-tolyl [1,1'-biphenyl]-2-carbothioate (1f)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1f** as a white solid. 70% yield (2.13 g); m.p. 83-84 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.56-7.51 (m, 1H), 7.47-7.32 (m, 7H), 7.23-7.14 (m, 4H), 2.34 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 194.16, 140.46, 140.17, 139.79, 138.53, 134.50, 131.29, 130.90, 130.14, 129.14, 128.39, 127.86, 127.74, 127.35, 124.53, 21.47. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>16</sub>OS 304.0916; Found 304.0915.

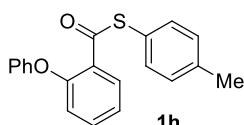
### *S-p-tolyl 2-methoxybenzothioate (1g)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1g** as a white solid. 52% yield (1.34 g); m.p. 54-55 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.85 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.54-7.45 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 8.3 Hz, 2H), 3.96 (s, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 189.78, 158.27, 139.63, 135.02, 134.06, 130.07, 126.47, 125.30, 120.62, 112.16, 55.95, 21.52. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>S 258.0709; Found 258.0712.

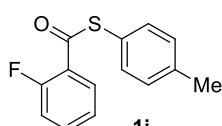
### *S*-*p*-tolyl 2-phenoxybenzothioate (**1h**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1h** as a white solid. 57% yield (1.82 g); m.p. 130-131 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.96-7.87 (m, 1H), 7.48-7.42 (m, 1H), 7.41-7.31 (m, 4H), 7.25-7.13 (m, 4H), 7.12-7.04 (m, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 2.37 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 189.55, 156.59, 155.75, 139.76, 134.99, 133.84, 130.10, 130.05, 129.99, 129.09, 124.78, 123.97, 123.45, 119.79, 119.34, 21.51. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>S 320.0866; Found 320.0871.

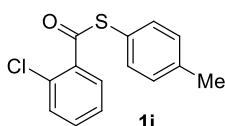
### *S*-*p*-tolyl 2-fluorobenzothioate (**1i**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1i** as a white solid. 64% yield (1.58 g); m.p. 51-52 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.96-7.85 (m, 1H), 7.59-7.49 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.29-7.23 (m, 3H), 7.22-7.15 (m, 1H), 2.41 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 187.81 (d, *J* = 5.2 Hz), 160.62 (d, *J* = 258.1 Hz), 140.17, 135.05, 134.67 (d, *J* = 8.7 Hz), 130.27, 130.03, 125.31 (d, *J* = 11.7 Hz), 124.44 (d, *J* = 3.6 Hz), 123.79 (d, *J* = 4.3 Hz), 117.08 (d, *J* = 22.3 Hz), 21.55. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -109.75. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>11</sub>FOS 246.0509; Found 246.0513.

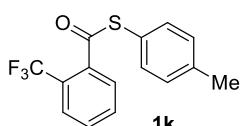
### *S*-*p*-tolyl 2-chlorobenzothioate (**1j**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1j** as a white solid. 61% yield (1.60 g); m.p. 82-83 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.49-7.38 (m, 4H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 190.80, 140.21, 137.27, 134.74, 132.46, 131.13, 131.01, 130.33, 129.25, 126.83, 123.93, 21.53. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>11</sub>ClOS 262.0214; Found 262.0231.

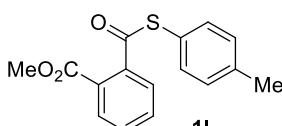
### *S*-*p*-tolyl 2-(trifluoromethyl)benzothioate (**1k**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1k** as a white solid. 69% yield (2.04 g); m.p. 87-88 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83-7.73 (m, 2H), 7.67-7.57 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 191.84, 140.37, 137.61, 134.67, 131.89, 131.28, 130.41, 128.52, 127.48 (q, *J* = 32.8 Hz), 127.15 (q, *J* = 5.1 Hz), 123.72, 123.35 (q, *J* = 272.5 Hz), 21.53. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -58.54. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>OS 296.0477; Found 296.0476.

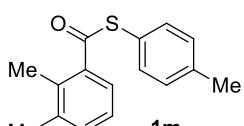
### methyl 2-((*p*-tolylthio)carbonyl)benzoate (**1l**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1l** as a white solid. 67% yield (1.92 g); m.p. 52-53 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.88 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.67 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.61-7.53 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 193.00, 166.97, 140.08, 139.85, 134.66, 131.84, 131.06, 130.33, 130.19, 129.49, 127.57, 124.14, 52.79, 21.54. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>S 286.0658; Found 286.0647.

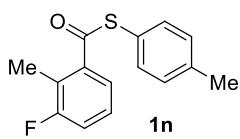
### *S*-*p*-tolyl 2,3-dimethylbenzothioate (**1m**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 20:1) afforded **1m** as a white solid. 49% yield (1.25 g); m.p. 77-78 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.7 Hz, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 194.24, 139.87, 138.46, 138.42, 134.86, 134.82, 133.16, 130.25, 125.87, 125.48, 125.00, 21.53, 20.56, 16.34. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>OS 256.0916; Found 256.0931.

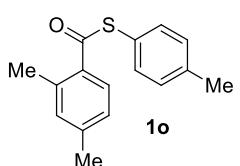
### *S-p-tolyl 3-fluoro-2-methylbenzothioate (1n)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 20:1) afforded **1n** as a white solid. 44% yield (1.14 g); m.p. 72-73 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30-7.22 (m, 3H), 7.18 (t, *J* = 8.5 Hz, 1H), 2.40 (s, 3H), 7.37 (d, *J* = 1.9 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.26, 161.54 (d, *J* = 245.9 Hz), 140.13, 139.32 (d, *J* = 3.9 Hz), 134.86, 130.32, 126.96 (d, *J* = 8.8 Hz), 124.42 (d, *J* = 18.7 Hz), 124.30, 124.04 (d, *J* = 3.7 Hz), 118.66 (d, *J* = 23.8 Hz), 21.53, 11.54 (d, *J* = 5.1 Hz). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -114.71. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>FOS 260.0666; Found 260.0668.

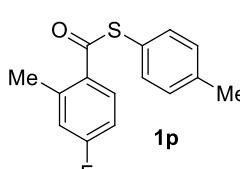
### *S-p-tolyl 2,4-dimethylbenzothioate (1o)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1o** as a white solid. 52% yield (1.33 g); m.p. 51-52 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.89 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.39 (dd, *J* = 8.1, 2.0 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.15-7.04 (m, 2H), 2.46 (d, *J* = 2.2 Hz, 3H), 2.39 (s, 3H), 2.36 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.13, 142.81, 139.73, 137.90, 135.07, 133.90, 132.74, 130.18, 129.19, 126.59, 124.93, 21.56, 21.51, 21.12. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>OS 256.0916; Found 256.0926.

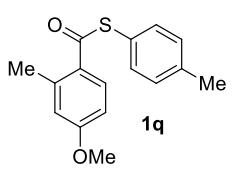
### *S-p-tolyl 4-fluoro-2-methylbenzothioate (1p)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1p** as a white solid. 55% yield (1.43 g); m.p. 75-76 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 8.4, 5.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.02-6.93 (m, 2H), 2.49 (s, 3H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 191.54, 164.59 (d, *J* = 253.6 Hz), 141.38 (d, *J* = 8.7 Hz), 140.04, 135.03, 133.05, 131.39 (d, *J* = 8.7 Hz), 130.30, 124.49, 118.79 (d, *J* = 21.5 Hz), 112.92 (d, *J* = 21.7 Hz), 21.54, 21.22. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -107.13. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>FOS 260.0666; Found 260.0674.

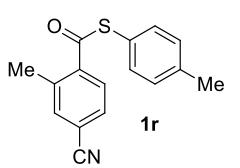
### *S-p-tolyl 4-methoxy-2-methylbenzothioate (1q)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1q** as a white solid. 58% yield (1.58 g); m.p. 70-71 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.82-6.73 (m, 2H), 3.85 (s, 3H), 2.50 (s, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 190.85, 162.53, 141.08, 139.69, 135.21, 131.67, 130.17, 129.06, 125.05, 117.40, 110.91, 55.51, 21.87, 21.52. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>S 272.0866; Found 272.0858.

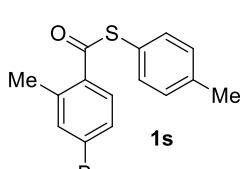
### *S-p-tolyl 4-cyano-2-methylbenzothioate (1r)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1r** as a white solid. 50% yield (1.33 g); m.p. 113-114 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.49 (s, 3H), 2.41 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.27, 140.97, 140.50, 138.26, 135.00, 134.79, 130.45, 129.71, 128.74, 123.52, 118.08, 115.23, 21.55, 20.34. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>13</sub>NOS 267.0712; Found 267.0712.

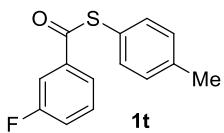
### *S-p-tolyl 4-bromo-2-methylbenzothioate (1s)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1s** as a white solid. 44% yield (1.41 g); m.p. 73-74 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.82-7.77 (m, 1H), 7.46-7.41 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.02, 140.09, 139.72, 135.66, 134.94, 134.74, 130.30, 130.16, 129.10, 126.69, 124.24, 21.53, 20.75. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>BrOS 319.9865; Found 319.9866.

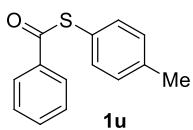
### **S-p-tolyl 3-fluorobenzothioate (1t)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1z** as a white solid. 66% yield (1.63 g); m.p. 69-70 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.81 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.68 (dt, *J* = 9.2, 2.0 Hz, 1H), 7.43 (td, *J* = 8.0, 5.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.31-7.22 (m, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 189.56, 162.75 (d, *J* = 248.5 Hz), 140.15, 138.69 (d, *J* = 6.6 Hz), 135.03, 130.48 (d, *J* = 7.7 Hz), 130.28, 123.32, 123.29, 120.60 (d, *J* = 21.4 Hz), 114.35 (d, *J* = 23.0 Hz), 21.47. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -111.32. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>11</sub>FOS 246.0509; Found 246.0505.

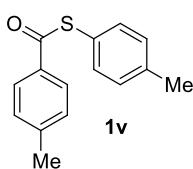
### **S-p-tolyl benzothioate (1u)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1aa** as a white solid. 51% yield (1.16 g); m.p. 108-109 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.02 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.59 (tt, *J* = 7.1, 1.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 190.72, 139.93, 136.77, 135.14, 133.70, 130.23, 128.83, 127.57, 123.82, 21.51. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>12</sub>OS 228.0603; Found 228.0597.

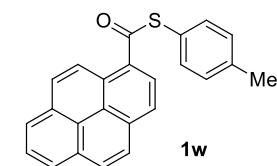
### **S-p-tolyl 4-methylbenzothioate (1v)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1ab** as a white solid. 49% yield (1.19 g); m.p. 113-114 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.26 (dd, *J* = 8.0, 4.1 Hz, 4H), 2.41 (s, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 190.27, 144.59, 139.81, 135.17, 134.24, 130.18, 129.48, 127.65, 124.04, 21.84, 21.50. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>14</sub>OS 242.0760; Found 242.0752.

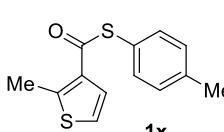
### **S-p-tolyl pyrene-1-carbothioate (1w)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1t** as a yellow solid. 42% yield (1.48 g); m.p. 176-177 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.84 (d, *J* = 9.3 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.21-8.05 (m, 5H), 7.99 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.96, 139.97, 135.11, 134.33, 131.04, 130.77, 130.54, 130.31, 129.92, 129.83, 128.75, 127.11, 126.58, 126.54, 126.28, 125.12, 124.84, 124.43, 124.19, 124.16, 21.58. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>16</sub>OS 352.0916; Found 352.0903.

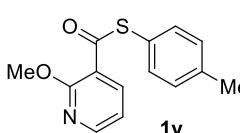
### **S-p-tolyl 2-methylthiophene-3-carbothioate (1x)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1u** as a white solid. 54% yield (1.34 g); m.p. 56-57 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 5.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 5.5 Hz, 1H), 2.69 (s, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 185.07, 148.37, 139.86, 135.19, 134.12, 130.18, 127.75, 124.19, 121.89, 21.50, 15.88. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>12</sub>OS<sub>2</sub> 248.0324; Found 248.0321.

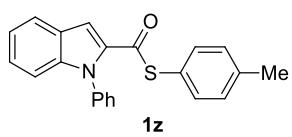
### **S-p-tolyl 2-methoxypyridine-3-carbothioate (1y)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **1v** as a white solid. 39% yield (1.01 g); m.p. 47-48 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.33 (dd, *J* = 4.9, 2.0 Hz, 1H), 8.17 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.99 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.11 (s, 3H), 2.40 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 188.95, 161.45, 151.11, 139.91, 139.27, 134.99, 130.16, 124.65, 120.32, 116.90, 54.11, 21.52. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>S 259.0662; Found 259.0674.

### *S-p-tolyl 1-phenyl-1*H*-indole-2-carbothioate (1z)*

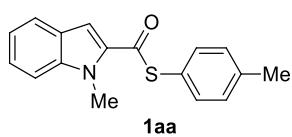


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **1w** as a white solid. 42% yield (1.44 g); m.p. 114-115 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.49-7.42 (m, 2H), 7.42-7.37 (m, 1H), 7.37-7.28 (m, 5H), 7.24-7.17 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 2.34 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 181.97, 141.05, 139.82, 138.15, 135.20, 134.40, 130.14, 129.27, 128.23, 127.98, 126.42, 126.24, 123.75, 122.83, 121.72, 112.04, 111.76, 21.47. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>17</sub>NOS 343.1025; Found 343.1026.

### *S-p-tolyl 1-methyl-1*H*-indole-2-carbothioate (1aa)*

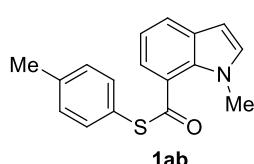


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1x** as a white solid. 44% yield (1.34 g); m.p. 145-146 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.56 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.40-7.33 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.19-7.14 (m, 1H), 3.97 (s, 3H), 2.40 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 183.79, 140.07, 140.01, 135.38, 133.45, 130.22, 126.05, 126.03, 123.88, 123.00, 121.02, 110.83, 110.45, 32.02, 21.52. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>NOS 281.0869; Found 281.0861.

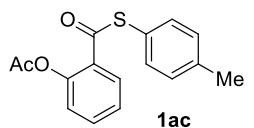
### *S-p-tolyl 1-methyl-1*H*-indole-7-carbothioate (1ab)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **1y** as a white solid. 32% yield (900 mg); m.p. 83-84 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.79 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 3.2 Hz, 1H), 6.53 (d, *J* = 3.2 Hz, 1H), 3.74 (s, 3H), 2.39 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.34, 139.92, 134.74, 132.06, 131.22, 130.30, 125.67, 125.04, 123.60, 118.46, 101.61, 37.30, 21.54. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>15</sub>NOS 281.0869; Found 281.0880.

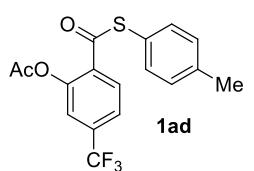
### *2-((p-tolylthio)carbonyl)phenyl acetate (1ac)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **1ac** as a white solid. 52% yield (1.49 g); m.p. 80-82 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.04 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.58 (td, *J* = 7.8, 1.7 Hz, 1H), 7.40-7.32 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 188.78, 169.55, 148.21, 140.12, 135.06, 133.90, 130.30, 130.00, 129.94, 126.34, 124.21, 123.93, 21.56, 21.32. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>S 286.0658; Found 286.0645.

### *2-((p-tolylthio)carbonyl)-5-(trifluoromethyl)phenyl acetate (1ad)*



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **1ad** as a white solid. 55% yield (1.95 g); m.p. 67-68 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 188.39, 169.02, 148.30, 140.52, 135.27 (q, *J* = 33.7 Hz), 134.95, 133.21, 130.44, 130.40, 123.22, 123.16 (q, *J* = 3.7 Hz), 122.99 (q, *J* = 271.5 Hz), 121.64 (q, *J* = 3.7 Hz), 21.55, 21.17. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -63.16. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S 354.0531; Found 354.0539.

### *S-p-tolyl 2-((2,3-dimethylphenyl)amino)benzothioate (1ae)*

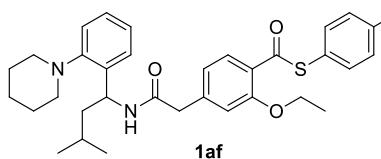


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 5:1) afforded **1ae** as a light yellow solid. 27% yield (936 mg); m.p. 111-112 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.31 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.48-7.38 (m, 2H), 7.32-7.24 (m, 3H), 7.10-6.98 (m, 3H), 6.77-6.62 (m, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 2.09 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 192.62, 147.89, 139.98, 138.33, 138.15, 135.77, 134.89, 132.99, 130.67, 130.23,

127.36, 126.10, 124.36, 123.78, 117.74, 116.26, 114.37, 21.55, 20.71, 14.23. **HRMS** (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>NOS 348.1422; Found 348.1424.

**S-p-tolyl-2-ethoxy-4-(2-((3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)amino)-2-oxoethyl)benzothioate (1af)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 3:1) afforded **1af** as a white solid. 35% yield (1.95 g); m.p. 101-102 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.26-7.18 (m, 4H), 7.11-7.04 (m, 2H), 6.89 (s, 1H), 6.86 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.78 (br, 1H), 5.37 (q, *J* = 8.5 Hz, 1H), 4.11 (qd, *J* = 16.2, 7.0 Hz, 2H), 3.54 (s, 2H), 2.93 (br, 2H), 2.62 (br, 2H), 2.39 (s, 3H), 1.75-1.67 (m, 2H), 1.66-1.46 (m, 9H), 1.41 (dt, *J* = 13.3, 6.6 Hz, 1H), 0.92 (dd, *J* = 6.5, 2.1 Hz, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 189.32, 168.71, 158.35, 152.65, 142.02, 139.57, 138.72, 135.06, 130.63, 130.05, 128.09, 127.96, 125.56, 125.26, 125.23, 123.05, 121.31, 113.67, 65.06, 50.12, 46.76, 44.37, 26.89, 25.47, 24.25, 22.89, 22.69, 21.52, 14.83. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub>S 558.2911; Found 558.2906.

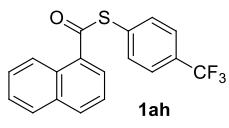
**S-(4-chlorophenyl) naphthalene-1-carbothioate (1ag)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1ag** as a white solid. 58% yield (1.73 g); m.p. 108-109 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.52 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.20 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.61-7.48 (m, 5H), 7.46 (d, *J* = 8.6 Hz, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 191.73, 136.28, 136.12, 134.35, 133.93, 133.70, 129.69, 129.41, 128.54, 128.38, 128.28, 126.93, 126.85, 125.30, 124.58. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>11</sub>ClOS 298.0214; Found 298.0206.

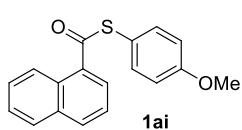
**S-(4-(trifluoromethyl)phenyl) naphthalene-1-carbothioate (1ah)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1ah** as a white solid. 42% yield (1.40 g); m.p. 101-102 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.53 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.22 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.75-7.67 (m, 4H), 7.62-7.50 (m, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 190.90, 135.15, 134.15, 133.96, 133.93, 133.10, 131.52 (d, *J* = 32.8 Hz), 129.41, 128.59, 128.50, 128.42, 127.00, 126.17 (d, *J* = 3.8 Hz), 125.23, 124.58, 123.98 (d, *J* = 271.2 Hz). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.78. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>11</sub>F<sub>3</sub>OS 322.0477; Found 322.0485.

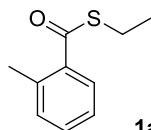
**S-(4-methoxyphenyl) naphthalene-1-carbothioate (1ai)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **1ai** as a white solid. 47% yield (1.38 g); m.p. 92-93 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.53 (d, *J* = 8.3 Hz, 1H), 8.21 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.59-7.48 (m, 5H), 7.03 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 193.37, 160.94, 136.65, 134.80, 133.96, 133.33, 129.47, 128.48, 128.19, 128.08, 126.82, 125.47, 124.61, 119.06, 115.14, 55.54. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>S 294.0709; Found 294.0691.

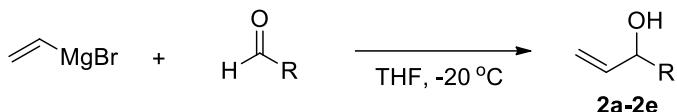
**S-ethyl 2-methylbenzothioate (1aj)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 20:1) afforded **1aj** as a colorless oil. 42% yield (757 mg).

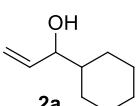
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.75 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 2H), 3.01 (q, *J* = 7.4 Hz, 2H), 2.47 (s, 3H), 1.33 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 194.35, 137.67, 136.63, 131.49, 131.48, 128.37, 125.69, 23.96, 20.55, 14.77. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>12</sub>OS 180.0603; Found 180.0607.

### 3.2 Procedure for synthesis of alkenyl alcohols 2a-2e



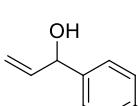
To a solution of corresponding aldehyde (10 mmol) in anhydrous THF (30 mL) was added Vinylmagnesium bromide solution (12 mL, 1M in THF). The reaction mixture was stirred at -20 °C for 1h. After the complete consumption of aldehyde was confirmed by TLC, the reaction mixture was quenched with water (20 mL) and extracted with EtOAc (40 mLx2). The organic layer was washed with brine (40 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel to yield the desired product **2a-2e**.

#### **1-cyclohexylprop-2-en-1-ol (2a)**

 Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 8:1) afforded **2a** as a colorless oil. Known compound. 97% yield (1.36 g).

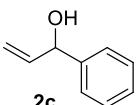
**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.86 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.26-5.07 (m, 2H), 3.85 (t, *J* = 6.5 Hz, 1H), 1.88-1.82 (m, 1H), 1.79-1.72 (m, 2H), 1.70-1.63 (m, 2H), 1.58 (br, 1H), 1.45-1.36 (m, 1H), 1.28-1.11 (m, 3H), 1.06-0.94 (m, 2H).

#### **1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (2b)**

 Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 8:1) afforded **2b** as a colorless oil. Known compound. 89% yield (1.8 g).

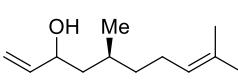
**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 5.98 (ddd, *J* = 16.8, 10.4, 6.1 Hz, 1H), 5.39-5.31 (m, 1H), 5.26-5.18 (m, 2H), 2.49 (br, 1H).

#### **1-phenylprop-2-en-1-ol (2c)**

 Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 8:1) afforded **2c** as a colorless oil. Known compound. 92% yield (1.23 g).

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.38-7.32 (m, 4H), 7.31-7.25 (m, 1H), 6.03 (ddd, *J* = 17.2, 10.1, 6.1 Hz, 1H), 5.36-5.30 (m, 1H), 5.21-5.13 (m, 2H), 2.23 (br, 1H).

#### **(5S)-5,9-dimethyldeca-1,8-dien-3-ol (2d)**

 Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **2d** as a colorless oil. 73% yield (1.33 g).

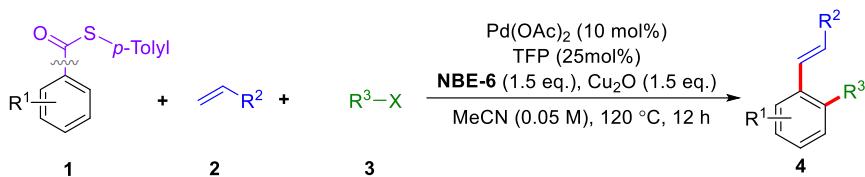
**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.96-5.75 (m, 1H), 5.22 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.15-5.03 (m, 2H), 4.26-4.12 (m, 1H), 2.06-1.89 (m, 2H), 1.71-1.64 (m, 4H), 1.60 (s, 3H), 1.58-1.52 (m, 1H), 1.49-1.12 (m, 4H), 0.93 (t, *J* = 6.4 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.99, 141.55, 131.35, 124.84, 114.82, 114.21, 71.77, 71.13, 44.56, 44.49, 37.66, 37.10, 29.20, 28.90, 25.84, 25.52, 25.45, 20.04, 19.36, 17.77. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>22</sub>O 182.1665; Found 182.1687.

#### **5-(4-(*tert*-butyl)phenyl)-4-methylpent-1-en-3-ol (2e)**

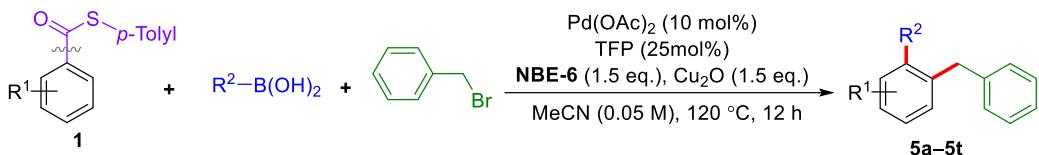
 Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 8:1) afforded **2e** as a colorless oil. Known compound. 85% yield (1.97 g).

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.30 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.11 (dd, *J* = 8.0, 5.1 Hz, 2H), 5.99-5.83 (m, 1H), 5.33-5.10 (m, 2H), 4.12-3.89 (m, 1H), 3.80-3.66 (m, 0.4H), 2.90-2.77 (m, 1H), 2.43-2.28 (m, 1H), 1.96-1.87 (m, 1H), 1.87-1.81 (m, 0.4H), 1.31 (s, 9H), 0.86 (dd, *J* = 9.3, 6.8 Hz, 3H).

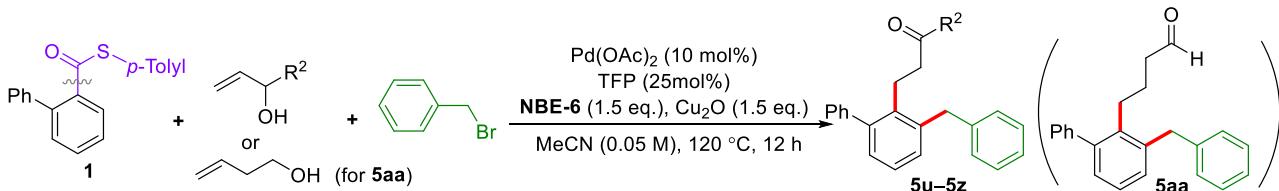
#### 4. Modular *ipso*-*ortho* difunctionalization of aromatic thioesters via Pd/NBE strategy



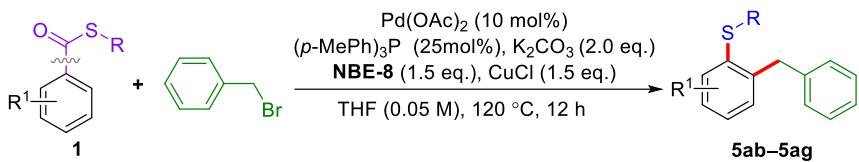
A oven dried 25 mL Schlenk tube was charged with thioester **1** (0.1 mmol, 1eq.), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol, 0.1 eq.), TFP (5.8 mg, 0.025 mmol, 0.25 eq.), **NBE-6** (38.7 mg, 0.15 mmol, 1.5 eq.), Cu<sub>2</sub>O (21.5 mg, 0.15 mmol, 1.5 eq.), alkene **2** (0.15 mmol, 1.5 eq.), benzyl bromides or alkyl iodides **3** (0.3 mmol, 3.0 eq.) and 2.0 mL MeCN. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for 12 h under N<sub>2</sub> atmosphere. Then the reaction mixture was cooled to room temperature, EtOAc (5 mL) and ammonium hydroxide (3 mL) were added, and the resulting mixture was continuously stirred at room temperature for another 30 min. The mixture was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/Hexane) to afford the products **4**.



A oven dried 25 mL Schlenk tube was charged with thioester **1** (0.1 mmol, 1eq.), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol, 0.1 eq.), TFP (5.8 mg, 0.025 mmol, 0.25 eq.), **NBE-6** (38.7 mg, 0.15 mmol, 1.5 eq.), Cu<sub>2</sub>O (21.5 mg, 0.15 mmol, 1.5 eq.), boronic acid (0.15 mmol, 1.5 eq.), benzyl bromide (0.3 mmol, 3.0 eq.) and 2.0 mL MeCN. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for 12 h under N<sub>2</sub> atmosphere. Then the reaction mixture was cooled to room temperature, EtOAc (5 mL) and ammonium hydroxide (3 mL) were added, and the resulting mixture was continuously stirred at room temperature for another 30 min. The mixture was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/Hexane) to afford the products **5a-5t**.



A oven dried 25 mL Schlenk tube was charged with thioester **1** (0.1 mmol, 1eq.), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol, 0.1 eq.), TFP (5.8 mg, 0.025 mmol, 0.25 eq.), **NBE-6** (38.7 mg, 0.15 mmol, 1.5 eq.), Cu<sub>2</sub>O (21.5 mg, 0.15 mmol, 1.5 eq.), allylic alcohol (0.15 mmol, 1.5 eq.), benzyl bromide (0.3 mmol, 3.0 eq.) and 2.0 mL MeCN. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for 12 h under N<sub>2</sub> atmosphere. Then the reaction mixture was cooled to room temperature, EtOAc (5 mL) and ammonium hydroxide (3 mL) were added, and the resulting mixture was continuously stirred at room temperature for another 30 min. The mixture was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/Hexane) to afford the products **5u-5aa**.



A oven dried 25 mL Schlenk tube was charged with thioester **1** (0.1 mmol, 1 eq.), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol, 0.1 eq.), (*p*-MePh)<sub>3</sub>P (7.6 mg, 0.025 mmol, 0.25 eq.), **NBE-8** (32.0 mg, 0.15 mmol, 1.5 eq.), CuCl (14.8 mg, 0.15 mmol, 1.5 eq.), K<sub>2</sub>CO<sub>3</sub> (27.6 mg, 0.2 mmol, 2.0 eq.), benzyl bromide (0.3 mmol, 3.0 eq.) and 2.0 mL THF. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for 12 h under N<sub>2</sub> atmosphere. Then the reaction mixture was cooled to room temperature, EtOAc (5 mL) and ammonium hydroxide (3 mL) were added, and the resulting mixture was continuously stirred at room temperature for another 30 min. The mixture was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/Hexane) to afford the products **5ab-5ag**.

### (E)-ethyl 3-(2-benzylnaphthalen-1-yl)acrylate (4a)

**4a** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4a** as a white solid. 82% yield (25.9 mg). m.p. 71-72 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 16.3 Hz, 1H), 8.08-8.01 (m, 1H), 7.82 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.49 (td, *J* = 7.7, 1.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.28-7.24 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.15-7.10 (m, 2H), 6.18 (d, *J* = 16.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.20 (s, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.49, 142.67, 140.66, 136.54, 132.42, 131.66, 131.57, 128.98, 128.91, 128.63, 128.56, 128.42, 126.74, 126.29, 126.22, 125.77, 125.24, 60.83, 39.76, 14.47. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub> 316.1458; Found 316.1438.

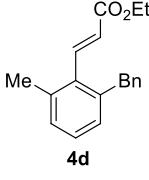
### (E)-ethyl 3-(2-benzyl-4-methylnaphthalen-1-yl)acrylate (4b)

**4b** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4b** as a white solid. 70% yield (23.1 mg). m.p. 72-73 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 16.3 Hz, 1H), 8.09-8.05 (m, 1H), 8.01-7.96 (m, 1H), 7.54-7.49 (m, 2H), 7.28-7.25 (m, 2H), 7.21-7.16 (m, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 6.15 (d, *J* = 16.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.18 (s, 2H), 2.64 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.62, 142.91, 140.80, 136.11, 135.39, 131.71, 131.64, 129.98, 129.47, 128.93, 128.60, 126.39, 126.22, 125.80, 125.63, 124.54, 60.77, 39.65, 19.72, 14.47. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>2</sub> 330.1614; Found 330.1617.

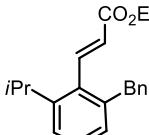
### (E)-ethyl 3-(2-benzyl-4-methoxynaphthalen-1-yl)acrylate (4c)

**4c** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 45:1) afforded **4c** as a white solid. 58% yield (20.1 mg). m.p. 70-71 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 16.2 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.56-7.44 (m, 2H), 7.31-7.25 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 6.64 (s, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.22 (s, 2H), 3.92 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.86, 155.83, 142.55, 140.67, 137.43, 132.71, 128.87, 128.64, 127.35, 126.29, 125.18, 125.00, 124.85, 124.78, 124.08, 122.34, 106.68, 60.68, 55.65, 40.22, 14.49. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub> 346.1563; Found 346.1564.

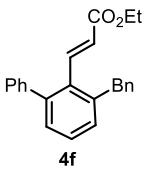
**(E)-ethyl 3-(2-benzyl-6-methylphenyl)acrylate (4d)**

  
**4d** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4d** as a white solid. 75% yield (21.0 mg). m.p. 63-64 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 16.3 Hz, 1H), 7.28-7.24 (m, 2H), 7.21-7.14 (m, 2H), 7.13-7.07 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.96 (d, *J* = 16.4 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 2H), 2.33 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.63, 143.46, 140.60, 139.34, 136.66, 134.56, 129.01, 128.86, 128.55, 128.38, 128.24, 126.19, 124.57, 60.65, 39.91, 21.28, 14.43. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub> 280.1458; Found 280.1477.

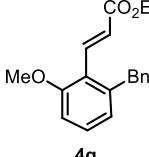
**(E)-ethyl 3-(2-benzyl-6-isopropylphenyl)acrylate (4e)**

  
**4e** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4e** as a white solid. 81% yield (24.9 mg). m.p. 60-61 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 16.3 Hz, 1H), 7.27-7.22 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 7.00 (dd, *J* = 7.0, 1.7 Hz, 1H), 5.88 (d, *J* = 16.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 3.12 (hept, *J* = 6.8 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 6H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.40, 147.13, 144.01, 140.68, 138.62, 133.97, 129.10, 128.52, 128.47, 127.79, 126.14, 125.02, 123.62, 60.69, 40.10, 30.12, 24.03, 14.43. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub> 308.1771; Found 308.1773.

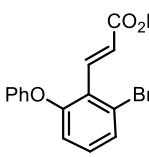
**(E)-ethyl 3-(3-benzyl-[1,1'-biphenyl]-2-yl)acrylate (4f)**

  
**4f** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **4f** as a white solid. 83% yield (28.4 mg). m.p. 69-70 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 16.3 Hz, 1H), 7.38-7.25 (m, 8H), 7.24-7.13 (m, 5H), 5.63 (d, *J* = 16.3 Hz, 1H), 4.15-4.08 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.46, 143.28, 142.44, 141.25, 140.48, 139.75, 133.28, 129.88, 129.05, 128.96, 128.64, 128.55, 128.25, 127.26, 126.29, 124.96, 60.43, 39.99, 14.33. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub> 342.1614; Found 342.1617.

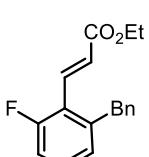
**(E)-ethyl 3-(2-benzyl-6-methoxyphenyl)acrylate (4g)**

  
**4g** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4g** as a white solid. 30% yield (8.9 mg). m.p. 70-71 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 16.1 Hz, 1H), 7.28-7.24 (m, 3H), 7.21-7.12 (m, 3H), 6.87-6.80 (m, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.13 (s, 2H), 3.87 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.97, 159.45, 142.30, 140.41, 138.60, 130.24, 128.84, 128.60, 126.25, 123.39, 122.83, 122.39, 109.39, 60.41, 55.60, 39.83, 14.47. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>3</sub> 296.1407; Found 296.1402.

**(E)-ethyl 3-(2-benzyl-6-phenoxyphenyl)acrylate (4h)**

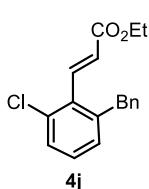
  
**4h** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4h** as a white solid. 80% yield (28.6 mg). m.p. 56-57 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 16.2 Hz, 1H), 7.37-7.27 (m, 4H), 7.23-7.15 (m, 4H), 7.14-7.09 (m, 1H), 7.02-6.93 (m, 3H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 16.2, 1H), 4.22-4.14 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.51, 156.91, 156.62, 142.54, 140.12, 137.94, 130.04, 129.98, 128.94, 128.70, 126.41, 125.77, 125.19, 123.86, 123.74, 119.32, 117.20, 60.50, 39.84, 14.42. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>3</sub> 358.1563; Found 358.1567.

**(E)-ethyl 3-(2-benzyl-6-fluorophenyl)acrylate (4i)**

  
**4i** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4i** as a white solid. 61% yield (17.3 mg). m.p. 69-70 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 16.2 Hz, 1H), 7.29-7.25 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16-7.10 (m, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 6.53 (dd, *J* = 16.2, 1.2 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.13 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.22, 162.09 (d, *J* = 253.5 Hz), 142.78 (d,

*J* = 2.4 Hz), 139.63, 135.96, 130.53 (d, *J* = 10.0 Hz), 128.82, 128.75, 126.56, 126.53, 124.34 (d, *J* = 13.8 Hz), 121.75 (d, *J* = 11.1 Hz), 114.59 (d, *J* = 23.3 Hz), 60.70, 39.45 (d, *J* = 2.6 Hz), 14.41. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -110.64. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>FO<sub>2</sub> 284.1207; Found 284.1199.

### (E)-ethyl 3-(2-benzyl-6-chlorophenyl)acrylate (4j)



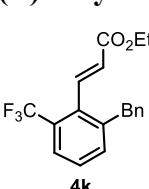
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4j** as a white solid. 40% yield (12.0 mg). m.p. 73-74 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 16.4 Hz, 1H), 7.33-7.26 (m, 3H), 7.23-7.17 (m, 2H), 7.09 (d, *J* = 7.4 Hz, 3H), 6.18 (d, *J* = 16.4 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.36, 141.42, 140.57, 139.86, 133.91, 133.55, 129.38, 129.20, 128.96,

128.73, 128.23, 126.51, 125.98, 60.83, 39.96, 14.41. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>ClO<sub>2</sub> 300.0912; Found 300.0933.

### (E)-ethyl 3-(2-benzyl-6-(trifluoromethyl)phenyl)acrylate (4k)

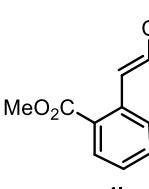


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **4k** as a white solid. 68% yield (22.7 mg). m.p. 77-79 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.85-7.77 (m, 1H), 7.62-7.57 (m, 1H), 7.39-7.34 (m, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 2H), 5.96 (d, *J* = 16.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 165.81, 140.75, 140.54, 139.62,

134.40, 133.84, 129.04, 128.92 (q, *J* = 32.5 Hz), 128.77, 128.19, 126.64, 126.58, 124.35 (q, *J* = 17.0 Hz), 124.06 (q, *J* = 271.2 Hz), 60.89, 39.48, 14.35. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -58.16. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>17</sub>F<sub>3</sub>O<sub>2</sub> 334.1175; Found 334.1176.

### (E)-methyl 3-benzyl-2-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (4l)

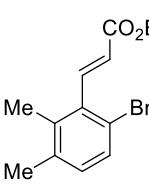


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 45:1) afforded **4l** as a white solid. 52% yield (16.8 mg). m.p. 68-70 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 16.2 Hz, 1H), 7.76-7.72 (m, 1H), 7.35-7.31 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.18 (m, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 5.82 (d, *J* = 16.3 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 3.84 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.24, 166.19, 143.99, 140.01, 139.85, 136.26, 134.00, 130.87, 129.04, 128.69, 128.33, 128.26, 126.43,

123.63, 60.70, 52.46, 39.48, 14.41. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> 324.1356; Found 324.1368.

### (E)-ethyl 3-(6-benzyl-2,3-dimethylphenyl)acrylate (4m)

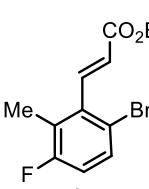


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4m** as a white solid. 86% yield (25.3 mg). m.p. 62-63 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 16.3 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12-7.04 (m, 3H), 6.93 (d, *J* = 7.7 Hz, 1H), 5.88 (d, *J* = 16.4 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.56,

144.58, 140.83, 136.60, 135.32, 135.00, 134.79, 129.85, 129.00, 128.50, 127.64, 126.09, 124.88, 60.61, 39.85, 20.55, 17.27, 14.42. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>4</sub> 294.1614; Found 294.1614.

### (E)-ethyl 3-(6-benzyl-3-fluoro-2-methylphenyl)acrylate (4n)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4n** as a white solid. 87% yield (25.9 mg). m.p. 63-65 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 16.3 Hz, 1H), 7.28-7.24 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H),

7.08 (d, *J* = 7.1 Hz, 2H), 7.00-6.92 (m, 2H), 5.94 (d, *J* = 16.4 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 2.23 (d, *J* = 2.4 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.30, 160.16 (d, *J* = 242.0 Hz), 142.42 (d, *J* = 3.0 Hz), 140.38, 136.57 (d, *J* = 5.0 Hz), 134.80 (d, *J* = 4.0 Hz), 128.94, 128.85, 128.62, 126.32, 125.59, 123.50 (d, *J* = 17.0 Hz), 114.91 (d, *J* = 23.0 Hz), 60.78, 39.45, 14.40, 12.50 (d, *J* = 5.0 Hz). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -117.87. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>19</sub>FO<sub>2</sub> 298.1364; Found 298.1414.

**(E)-ethyl 3-(2-benzyl-4,6-dimethylphenyl)acrylate (4o)**

**4o** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4o** as a white solid. 71% yield (20.9 mg). m.p. 79-80 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 16.3 Hz, 1H), 7.28-7.25 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.94 (s, 1H), 6.86 (s, 1H), 5.95 (d, *J* = 16.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 2.32 (s, 3H), 2.28 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.83, 143.45, 140.74, 139.45, 138.36, 136.78, 131.55, 129.85, 129.14, 128.97, 128.54, 126.15, 123.93, 60.58, 39.89, 21.34, 21.28, 14.44. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub> 294.1614; Found 294.1612.

**(E)-ethyl 3-(2-benzyl-4-fluoro-6-methylphenyl)acrylate (4p)**

**4p** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4p** as a white solid. 60% yield (17.9 mg). m.p. 66-67 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 16.3 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 6.82 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.71 (dd, *J* = 9.5, 2.7 Hz, 1H), 5.95 (d, *J* = 16.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 2H), 2.34 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.55, 162.28 (d, *J* = 247.8 Hz), 142.47, 142.05 (d, *J* = 7.9 Hz), 139.75, 139.30 (d, *J* = 8.1 Hz), 130.42 (d, *J* = 3.1 Hz), 129.04, 128.71, 126.50, 124.79, 115.57 (d, *J* = 21.0 Hz), 114.09 (d, *J* = 21.5 Hz), 60.73, 39.90, 21.46, 14.43. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -113.75. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>19</sub>FO<sub>2</sub> 298.1364; Found 298.1370.

**(E)-ethyl 3-(2-benzyl-4-methoxy-6-methylphenyl)acrylate (4q)**

**4q** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4q** as a white solid. 65% yield (20.1 mg). m.p. 69-70 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 16.3 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 2.6 Hz, 1H), 6.57 (d, *J* = 2.6 Hz, 1H), 5.94 (d, *J* = 16.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 3.76 (s, 3H), 2.36 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.04, 159.43, 142.93, 141.58, 140.35, 138.97, 128.97, 128.60, 126.82, 126.26, 123.03, 114.28, 114.16, 60.53, 55.27, 40.22, 21.95, 14.46. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub> 310.1563; Found 310.1565.

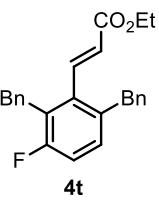
**(E)-ethyl 3-(2-benzyl-4-cyano-6-methylphenyl)acrylate (4r)**

**4r** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4r** as a white solid. 49% yield (14.9 mg). m.p. 72-73 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 16.4 Hz, 1H), 7.39 (s, 1H), 7.32-7.26 (m, 3H), 7.23 (t, *J* = 5.9 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 5.99 (d, *J* = 16.4 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 2.34 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 165.86, 141.49, 140.69, 139.64, 138.93, 137.83, 131.89, 131.28, 129.01, 128.87, 126.80, 126.37, 118.82, 111.89, 61.01, 39.55, 20.98, 14.36. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> 305.1410; Found 305.1428.

**(E)-ethyl 3-(2-benzyl-4-bromo-6-methylphenyl)acrylate (4s)**

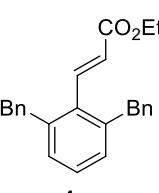
**4s** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4s** as a white solid. 62% yield (22.3 mg). m.p. 70-71 °C.  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 16.4 Hz, 1H), 7.30-7.26 (m, 3H), 7.23-7.14 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 5.95 (d, *J* = 16.4 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 2.31 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.35, 142.34, 141.43, 139.69, 138.76, 133.59, 131.67, 130.99, 128.98, 128.71, 126.51, 125.16, 122.37, 60.78, 39.69, 21.06, 14.41. HRMS (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>19</sub>BrO<sub>2</sub> 358.0563; Found 358.0554.

**(E)-ethyl 3-(2,6-dibenzyl-3-fluorophenyl)acrylate (4t)**



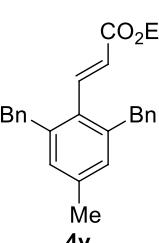
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4t** as a white solid. 49% yield (18.3 mg). m.p. 75-76 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 16.4 Hz, 1H), 7.28-7.24 (m, 4H), 7.21-7.15 (m, 2H), 7.12-6.99 (m, 6H), 5.79 (d, *J* = 16.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 2.1 Hz, 2H), 3.95 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.03, 160.09 (d, *J* = 243.0 Hz), 142.23 (d, *J* = 2.0 Hz), 140.36, 139.75, 137.16 (d, *J* = 4.0 Hz), 134.96 (d, *J* = 3.0 Hz), 129.95 (d, *J* = 9.0 Hz), 128.98, 128.66, 128.61, 128.40 (d, *J* = 1.0 Hz), 126.31 (d, *J* = 9.0 Hz), 126.20, 126.04, 125.79, 115.28 (d, *J* = 22.0 Hz), 60.73, 39.42, 32.27 (d, *J* = 4.0 Hz), 14.39. <sup>19</sup>**F NMR** (470 MHz, CDCl<sub>3</sub>) δ -118.08. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>23</sub>FO<sub>2</sub> 374.1677; Found 374.1669.

#### (E)-ethyl 3-(2,6-dibenzylphenyl)acrylate (**4u**)



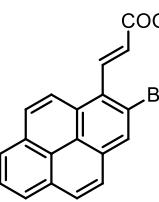
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4u** as a white solid. 30% yield (10.7 mg). m.p. 55-56 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 16.3 Hz, 1H), 7.29-7.25 (m, 4H), 7.22-7.16 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 4H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.84 (d, *J* = 16.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 4H), 1.30 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.31, 143.42, 140.59, 139.25, 135.06, 129.06, 128.66, 128.57, 128.40, 126.22, 125.05, 60.63, 39.90, 14.42. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>2</sub> 356.1771; Found 356.1769.

#### (E)-ethyl 3-(2,6-dibenzyl-4-methylphenyl)acrylate (**4v**)



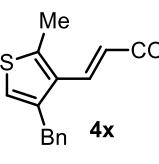
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4v** as a white solid. 27% yield (10.0 mg). m.p. 58-59 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 16.3 Hz, 1H), 7.28-7.26 (m, 4H), 7.20-7.16 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 4H), 6.88 (s, 2H), 5.83 (d, *J* = 16.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 4H), 2.26 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.48, 143.50, 140.78, 139.26, 138.33, 132.16, 129.61, 129.03, 128.57, 126.18, 124.58, 60.55, 39.87, 21.37, 14.42. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>26</sub>O<sub>2</sub> 370.1927; Found 370.1908.

#### (E)-ethyl 3-(2-benzylpyren-1-yl)acrylate (**4w**)



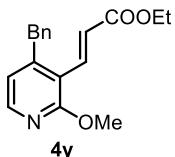
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4w** as a yellow solid. 62% yield (24.2 mg). m.p. 144-145 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 16.3 Hz, 1H), 8.32 (d, *J* = 9.3 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 2H), 8.08-8.04 (m, 2H), 8.00-7.95 (m, 3H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 3H), 6.28 (d, *J* = 16.3 Hz, 1H), 4.44 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.54, 143.03, 140.55, 136.92, 131.38, 131.24, 130.66, 130.23, 129.28, 129.19, 128.66, 128.30, 128.26, 127.24, 126.82, 126.53, 126.36, 126.14, 125.66, 125.40, 124.69, 123.82, 60.86, 40.56, 14.51. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>22</sub>O<sub>2</sub> 390.1614; Found 390.1624.

#### (E)-ethyl 3-(4-benzyl-2-methylthiophen-3-yl)acrylate (**4x**)

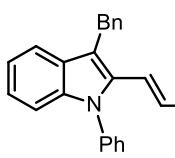


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4x** as a pale yellow solid. 47% yield (13.4 mg). m.p. 53-54 °C  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 16.2 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25-7.16 (m, 3H), 6.52 (s, 1H), 6.10 (d, *J* = 16.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 2.55 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.56, 142.30, 141.64, 139.43, 137.33, 131.60, 129.04, 128.67, 126.47, 119.33, 119.16, 60.54, 36.63, 15.74, 14.46. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S 286.1022; Found 286.1018.

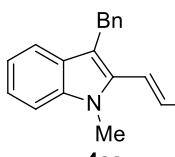
#### (E)-ethyl 3-(4-benzyl-2-methoxypyridin-3-yl)acrylate (**4y**)

  
**4y** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 35:1) afforded **4y** as a brown solid. 42% yield (12.5 mg). m.p. 91-92 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 5.2 Hz, 1H), 7.89 (d, *J* = 16.0 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.78-6.68 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.12 (s, 2H), 4.02 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.69, 162.86, 151.80, 146.88, 138.71, 136.40, 128.95, 128.86, 126.76, 123.66, 119.48, 116.72, 60.61, 53.93, 38.98, 14.47. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub> 297.1359; Found 297.1355.

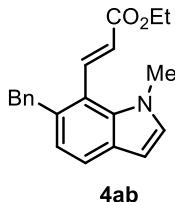
#### (E)-ethyl 3-(3-benzyl-1-phenyl-1H-indol-2-yl)acrylate (**4z**)

  
**4z** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 30:1) afforded **4z** as a pale yellow solid. 55% yield (21.0 mg). m.p. 71-72 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 16.2 Hz, 1H), 7.58-7.51 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 4.8 Hz, 4H), 7.23-7.17 (m, 2H), 7.13-7.08 (m, 2H), 5.66 (d, *J* = 16.3 Hz, 1H), 4.37 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.20, 140.39, 139.96, 138.02, 132.43, 131.97, 129.90, 128.68, 128.47, 128.44, 128.14, 126.25, 124.86, 120.82, 120.59, 120.23, 118.39, 110.76, 60.49, 30.96, 14.40. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>23</sub>NO<sub>2</sub> 381.1723; Found 381.1711.

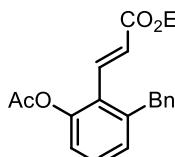
#### (E)-ethyl 3-(3-benzyl-1-methyl-1H-indol-2-yl)acrylate (**4aa**)

  
**4aa** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 30:1) afforded **4aa** as a white solid. 31% yield (9.9 mg). m.p. 84-85 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 16.2 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.34-7.27 (m, 2H), 7.25-7.21 (m, 2H), 7.21-7.13 (m, 3H), 7.09-7.05 (m, 1H), 6.24 (d, *J* = 16.2 Hz, 1H), 4.30 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 167.30, 140.58, 138.95, 132.54, 132.02, 128.62, 128.32, 127.91, 126.15, 124.33, 120.26, 120.06, 118.78, 118.56, 109.62, 60.71, 31.33, 30.97, 14.50. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub> 319.1567; Found 319.1572.

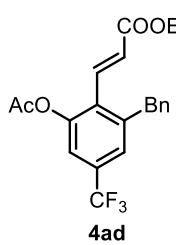
#### (E)-ethyl 3-(6-benzyl-1-methyl-1H-indol-7-yl)acrylate (**4ab**)

  
**4ab** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4ab** as a white solid. 40% yield (12.7 mg). m.p. 78-79 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 16.2 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.99-6.93 (m, 2H), 6.46 (d, *J* = 3.1 Hz, 1H), 5.96 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.13 (s, 2H), 3.81 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.45, 142.60, 141.77, 134.51, 132.70, 131.40, 128.88, 128.63, 128.47, 125.98, 125.39, 122.87, 121.47, 119.81, 101.24, 60.74, 39.29, 37.94, 14.45. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub> 319.1567; Found 319.1574.

#### (E)-ethyl 3-(2-acetoxy-6-benzylphenyl)acrylate (**4ac**)

  
**4ac** Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4ac** as a white solid. 60% yield (19.5 mg). m.p. 68-69 °C.  
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 16.3 Hz, 1H), 7.30-7.25 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.23 (d, *J* = 16.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 2.28 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 169.39, 166.56, 149.05, 141.80, 139.66, 138.36, 129.72, 129.01, 128.69, 128.35, 127.50, 126.47, 124.49, 121.30, 60.73, 39.66, 21.29, 14.40. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> 324.1356; Found 324.1346.

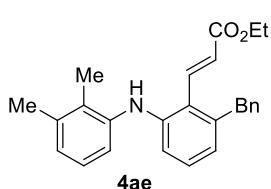
**(E)-ethyl 3-(2-acetoxy-6-benzyl-4-(trifluoromethyl)phenyl)acrylate (4ad)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4ad** as a white solid. 41% yield (16.1 mg). m.p. 79-80 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 16.3 Hz, 1H), 7.35-7.26 (m, 4H), 7.25-7.20 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.23 (d, *J* = 16.3 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 2.29 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.92, 166.02, 149.00, 142.75, 138.57, 137.14, 131.53 (q, *J* = 32.5 Hz), 131.49, 128.93, 126.88, 126.15, 124.76 (q, *J* = 3.75 Hz), 123.36 (q, *J* = 271.2 Hz), 118.62 (q, *J* = 3.75 Hz), 61.00, 39.74, 21.15, 14.37. **19F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.82. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>F<sub>3</sub>O<sub>4</sub> 392.1230; Found 392.1203.

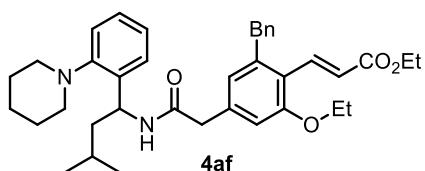
**(E)-ethyl 3-(2-benzyl-6-((2,3-dimethylphenyl)amino)phenyl)acrylate (4ae)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 8:1) afforded **4ae** as a pale yellow solid. 36% yield (13.8 mg). m.p. 71-72 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 16.4 Hz, 1H), 7.28-7.24 (m, 2H), 7.22-7.15 (m, 3H), 7.10-7.04 (m, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 7.5, 1H), 6.65 (d, *J* = 8.2, 1H), 6.32 (d, *J* = 16.4 Hz, 1H), 5.55 (br, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.03 (s, 2H), 2.32 (s, 3H), 2.11 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.84, 144.08, 141.32, 140.66, 140.49, 140.38, 138.23, 130.45, 129.59, 129.04, 128.60, 128.40, 126.27, 125.84, 123.83, 122.03, 121.83, 120.89, 113.99, 60.73, 40.08, 20.77, 14.42, 14.05. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>27</sub>NO<sub>2</sub> 385.2036; Found 385.2036.

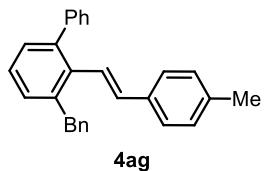
**(E)-ethyl 3-(2-benzyl-6-ethoxy-4-(2-((3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)amino)-2-oxoethyl)phenyl)acrylate (4af)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 3:1) afforded **4af** as a white solid. 45% yield (26.8 mg). m.p. 102-103 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 16.3 Hz, 1H), 7.26-7.15 (m, 5H), 7.11 (d, *J* = 5.6 Hz, 2H), 7.04 (d, *J* = 3.0 Hz, 2H), 6.76-6.59 (m, 4H), 5.36 (td, *J* = 6.9, 5.3 Hz, 1H), 4.22 (q, *J* = 5.7 Hz, 2H), 4.09 (s, 2H), 4.05-3.96 (m, 2H), 3.48 (s, 2H), 2.92 (br, 2H), 2.59 (br, 2H), 1.69-1.47 (m, 8H), 1.43 (t, *J* = 5.6 Hz, 3H), 1.41-1.36 (m, 1H), 1.31 (t, *J* = 5.7 Hz, 3H), 0.91 (dd, *J* = 5.2, 1.4 Hz, 6H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 169.23, 168.10, 159.23, 152.65, 142.80, 140.20, 138.86, 138.22, 137.73, 128.77, 128.65, 128.02, 127.81, 126.32, 125.17, 124.00, 122.90, 122.55, 121.14, 111.06, 64.25, 60.37, 49.84, 46.78, 44.38, 39.86, 26.82, 25.48, 24.27, 22.92, 22.68, 14.86, 14.49. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>48</sub>N<sub>2</sub>O<sub>4</sub> 596.3609; Found 596.3651.

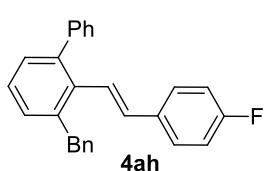
**(E)-3-benzyl-2-(4-methylstyryl)-1,1'-biphenyl (4ag)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **4ag** as a white solid. 89% yield (32.0 mg). m.p. 72-73 °C.

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.24 (m, 9H), 7.23-7.18 (m, 4H), 7.07-7.00 (m, 4H), 6.87 (d, *J* = 16.7 Hz, 1H), 6.23 (d, *J* = 16.7 Hz, 1H), 4.19 (s, 2H), 2.30 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 142.26, 141.93, 141.46, 139.09, 137.37, 136.29, 134.93, 134.83, 130.16, 130.07, 129.32, 129.02, 128.72, 128.59, 128.01, 126.94, 126.73, 126.25, 126.08, 125.87, 40.24, 21.33. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>24</sub> 360.1873; Found 360.1847.

**(E)-3-benzyl-2-(4-fluorostyryl)-1,1'-biphenyl (4ah)**

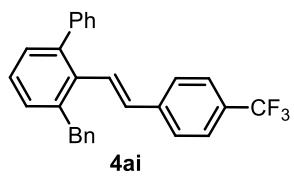


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **4ah** as a white solid. 90% yield (32.8 mg). m.p. 123-125 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.37-7.26 (m, 8H), 7.25-7.17 (m, 5H), 7.06 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.92 (t, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 16.7 Hz, 1H), 6.20 (d, *J* = 16.7 Hz, 1H), 4.18 (s, 2H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.34 (d, *J* = 246.9 Hz), 142.25, 142.05, 141.40, 139.07, 136.03, 133.86, 133.82 (d, *J* = 3.3 Hz), 130.15, 128.98, 128.78, 128.63, 128.05, 127.83, 127.75, 127.13, 126.81, 126.71 (d,

*J* = 3.3 Hz), 126.16, 115.52 (d, *J* = 21.6 Hz), 40.32. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -114.67. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>21</sub>F 364.1622; Found 364.1623.

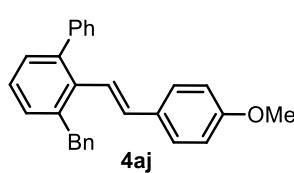
**(E)-3-benzyl-2-(4-(trifluoromethyl)styryl)-1,1'-biphenyl (4ai)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **4ai** as a white solid. 78% yield (32.3 mg). m.p. 126-127 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.36-7.26 (m, 9H), 7.25-7.14 (m, 6H), 7.00 (d, *J* = 16.7 Hz, 1H), 6.24 (d, *J* = 16.7 Hz, 1H), 4.18 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 142.18, 142.02, 141.23, 141.00, 139.11, 135.57, 133.61, 130.26, 130.11, 129.53, 129.21 (q, *J* = 32.5 Hz), 128.92, 128.87, 128.69, 128.13, 127.52, 126.96, 126.40, 126.25, 125.59 (q, *J* = 3.8 Hz), 124.32 (q, *J* = 270.1 Hz), 40.35. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.44. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>21</sub>F<sub>3</sub> 414.1590; Found 414.1583.

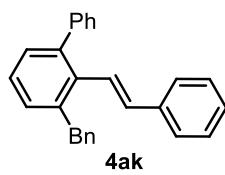
**(E)-3-benzyl-2-(4-methoxystyryl)-1,1'-biphenyl (4aj)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **4aj** as a white solid. 83% yield (31.2 mg). m.p. 105-106 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.38-7.24 (m, 9H), 7.23-7.18 (m, 4H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.80-6.74 (m, 3H), 6.20 (d, *J* = 16.7 Hz, 1H), 4.19 (s, 2H), 3.77 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 159.15, 142.31, 141.86, 141.50, 139.01, 136.36, 134.46, 130.43, 130.15, 130.09, 129.00, 128.71, 128.59, 128.00, 127.49, 126.83, 126.70, 126.07, 124.72, 114.00, 55.39, 40.25. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>24</sub>O 376.1822; Found 376.1822.

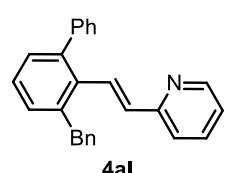
**(E)-3-benzyl-2-styryl-1,1'-biphenyl (4ak)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **4ak** as a white solid. 91% yield (31.5 mg). m.p. 87-88 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.39-7.24 (m, 10H), 7.23-7.16 (m, 6H), 7.14-7.11 (m, 2H), 6.92 (d, *J* = 16.7 Hz, 1H), 6.26 (d, *J* = 16.7 Hz, 1H), 4.19 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 142.19, 141.99, 141.42, 139.09, 137.61, 136.13, 135.02, 130.15, 130.11, 129.00, 128.74, 128.61, 128.04, 127.50, 127.07, 126.89, 126.78, 126.34, 126.12, 40.25. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>22</sub> 346.1716; Found 346.1724.

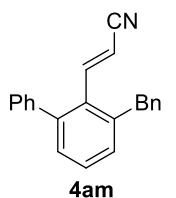
**(E)-2-(2-(3-benzyl-[1,1'-biphenyl]-2-yl)vinyl)pyridine (4al)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4al** as a pale yellow solid. 72% yield (25.0 mg). m.p. 92-93 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 4.2 Hz, 1H), 7.57-7.49 (m, 2H), 7.40-7.24 (m, 9H), 7.22-7.14 (m, 4H), 7.06 (dd, *J* = 7.8, 4.5 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.34 (d, *J* = 16.4 Hz, 1H), 4.22 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 155.56, 149.60, 142.09, 142.04, 141.14, 139.70, 136.49, 135.50, 134.70, 131.00, 130.12, 129.73, 129.22, 128.76, 128.56, 128.08, 127.44, 126.82, 126.10, 122.05, 121.74, 40.04. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>21</sub>N 347.1669; Found 347.1659.

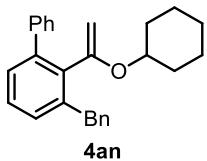
**(E)-3-(3-benzyl-[1,1'-biphenyl]-2-yl)acrylonitrile (4am)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4am** as a white solid. 93% yield (27.4 mg). m.p. 88-89 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.42-7.30 (m, 7H), 7.26-7.22 (m, 5H), 7.12 (d, *J* = 7.5 Hz, 2H), 5.06 (d, *J* = 17.0 Hz, 1H), 4.10 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 149.40, 142.65, 140.61, 140.04, 139.25, 132.25, 130.55, 129.77, 129.52, 129.36, 128.93, 128.66, 128.61, 127.74, 126.62, 117.82, 103.21, 40.01. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>17</sub>N 259.1356; Found 259.1353.

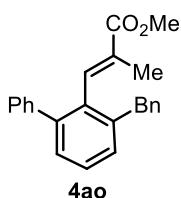
**3-benzyl-2-(1-(cyclohexyloxy)vinyl)-1,1'-biphenyl (4an)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4an** as a white solid. 53% yield (19.5 mg). m.p. 70-72 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.45 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.37-7.25 (m, 6H), 7.23 (t, *J* = 6.0 Hz, 2H), 7.21-7.16 (m, 2H), 7.05 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.17 (d, *J* = 2.2 Hz, 1H), 4.13 (s, 2H), 3.92 (tt, *J* = 9.0, 3.4 Hz, 1H), 3.84 (d, *J* = 2.3 Hz, 1H), 1.85 (br, 2H), 1.73-1.66 (m, 2H), 1.54-1.48 (m, 1H), 1.32-1.18 (m, 5H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 157.12, 142.34, 141.99, 141.68, 140.22, 137.03, 129.45, 129.24, 128.83, 128.40, 128.14, 127.84, 127.62, 126.73, 125.95, 87.68, 75.06, 38.79, 31.55, 25.82, 24.22. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>28</sub>O 368.2135; Found 368.2128.

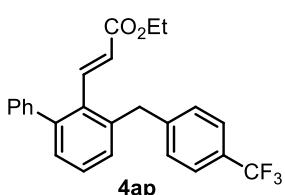
**(E)-methyl 3-(3-benzyl-[1,1'-biphenyl]-2-yl)-2-methylacrylate (4ao)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4ao** as a white solid. 73% yield (25.0 mg). m.p. 83-84 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.68 (s, 1H), 7.35-7.29 (m, 3H), 7.27-7.24 (m, 6H), 7.21-7.16 (m, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 3.97-3.89 (br, 2H), 3.70 (s, 3H), 1.21 (d, *J* = 1.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.13, 141.76, 141.59, 140.33, 139.52, 138.80, 134.16, 130.56, 129.35, 129.13, 129.00, 128.46, 128.39, 128.10, 128.00, 127.00, 126.18, 51.96, 40.07, 13.84. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub> 342.1614; Found 342.1612.

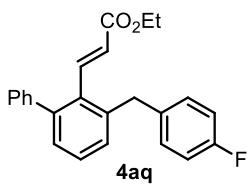
**(E)-ethyl 3-(3-(4-(trifluoromethyl)benzyl)-[1,1'-biphenyl]-2-yl)acrylate (4ap)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4ap** as a white solid. 62% yield (25.4 mg). m.p. 78-79 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 16.3 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.38-7.33 (m, 3H), 7.29-7.23 (m, 6H), 7.17 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.59 (d, *J* = 16.3 Hz, 1H), 4.18 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.33, 144.66, 143.01, 142.67, 141.03, 138.62, 133.39, 129.87, 129.86, 129.37, 129.31, 128.74, 128.62 (q, *J* = 31.3 Hz), 128.32, 127.39, 125.57 (q, *J* = 3.8 Hz), 125.21, 124.37 (q, *J* = 216.0 Hz), 60.54, 39.88, 14.30. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.33. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>21</sub>F<sub>3</sub>O<sub>2</sub> 410.1488; Found 410.1561.

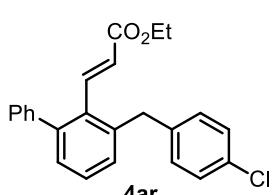
**(E)-ethyl 3-(3-(4-fluorobenzyl)-[1,1'-biphenyl]-2-yl)acrylate (4aq)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4aq** as a white solid. 52% yield (18.7 mg). m.p. 73-74 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 16.3 Hz, 1H), 7.39-7.29 (m, 4H), 7.28-7.24 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.10 (dd, *J* = 8.5, 5.4 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 5.60 (d, *J* = 16.3 Hz, 1H), 4.16-4.06 (m, 4H), 1.22 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.40, 161.57 (d, *J* = 244.3 Hz), 143.14, 142.62, 141.23, 139.59, 136.18 (d, *J* = 3.3 Hz), 133.34, 130.42 (d, *J* = 7.9 Hz), 129.88, 129.77, 129.13, 128.62, 128.29, 127.33, 125.09, 115.45 (d, *J* = 3.3 Hz), 60.46, 39.27, 14.34. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -117.09. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>21</sub>FO<sub>2</sub> 360.1520; Found 360.1517.

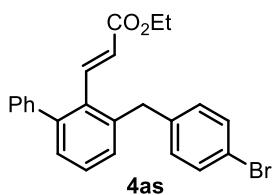
**(E)-ethyl 3-(3-(4-chlorobenzyl)-[1,1'-biphenyl]-2-yl)acrylate (4ar)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4ar** as a white solid. 67% yield (25.3 mg). m.p. 72-73°C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 16.3 Hz, 1H), 7.39-7.29 (m, 4H), 7.28-7.23 (m, 5H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 16.3 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.08 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.36, 143.07, 142.64, 141.17, 139.20, 139.02, 133.36, 132.13, 130.37, 129.87, 129.80, 129.20, 128.77, 128.64, 128.29, 127.35, 125.13, 60.48, 39.43, 14.34. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>21</sub>ClO<sub>2</sub> 376.1225; Found 376.1231.

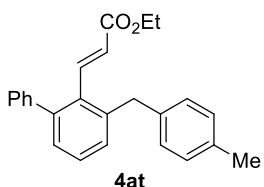
**(E)-ethyl 3-(3-(4-bromobenzyl)-[1,1'-biphenyl]-2-yl)acrylate (4as)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4as** as a white solid. 67% yield (28.2 mg). m.p. 64-65 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 16.3 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.38-7.29 (m, 4H), 7.27-7.24 (m, 3H), 7.15 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 16.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.37, 143.07, 142.61, 141.12, 139.52, 139.09, 133.32, 131.71, 130.77, 129.86, 129.79, 129.20, 128.65, 128.29, 127.34, 125.09, 120.17, 60.50, 39.47, 14.34. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>21</sub>BrO<sub>2</sub> 420.0719; Found 420.0716.

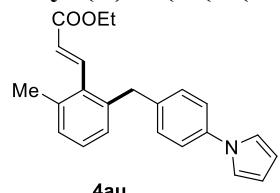
**(E)-ethyl 3-(3-(4-methylbenzyl)-[1,1'-biphenyl]-2-yl)acrylate (4at)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4at** as a white solid. 80% yield (28.5 mg). m.p. 71-72 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 16.3 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.33-7.25 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 5.63 (d, *J* = 16.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 2.32 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.50, 143.33, 142.44, 141.34, 140.10, 137.41, 135.78, 133.25, 129.90, 129.81, 129.35, 128.96, 128.88, 128.53, 128.24, 127.24, 124.94, 60.41, 39.59, 21.17, 14.35. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>2</sub> 356.1771; Found 356.1779.

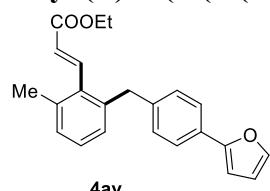
**ethyl (E)-3-(2-(4-(1H-pyrrol-1-yl)benzyl)-6-methylphenyl)acrylate (4au)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4au** as a white solid. 47% yield (16.2 mg). m.p. 71-72 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 16.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.19 (t, *J* = 6.0 Hz, 1H), 7.16-7.10 (m, 3H), 7.07-7.01 (m, 3H), 6.32 (t, *J* = 2.3 Hz, 2H), 5.97 (d, *J* = 16.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 2.35 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.62, 143.36, 139.08, 139.05, 138.12, 136.83, 134.58, 130.01, 129.06, 128.50, 128.21, 124.67, 120.70, 119.44, 110.33, 60.71, 39.32, 21.28, 14.43. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>23</sub>NO<sub>2</sub> 356.1771; Found 356.1779.

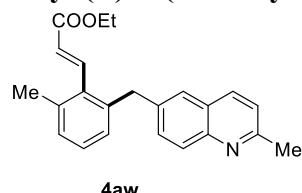
**ethyl (E)-3-(2-(4-(furan-2-yl)benzyl)-6-methylphenyl)acrylate (4av)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4av** as a white solid. 52% yield (18.9 mg). m.p. 76-78 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 16.3 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.14-7.07 (m, 3H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 3.4 Hz, 1H), 6.44 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.96 (d, *J* = 16.4 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 2H), 2.34 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.61, 154.11, 143.40, 141.95, 139.84, 139.16, 136.73, 134.58, 129.33, 128.99, 128.94, 128.42, 128.21, 124.62, 124.04, 111.70, 104.68, 60.66, 39.71, 21.26, 14.41. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub> 356.1771; Found 356.1779.

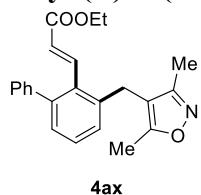
**ethyl (E)-3-(2-methyl-6-((2-methylquinolin-6-yl)methyl)phenyl)acrylate (4aw)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **4aw** as a white solid. 40% yield (13.8 mg). m.p. 81-82 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.93 (t, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 16.3 Hz, 1H), 7.50-7.40 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09-7.05 (m, 1H), 5.94 (d, *J* = 16.3 Hz, 1H), 4.24-4.16 (m, 4H), 2.73 (s, 3H), 2.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.58, 158.57, 146.75, 143.32, 138.82, 138.20, 136.88, 136.11, 134.70, 131.17, 129.11, 128.72, 128.51, 128.36, 126.85, 126.60, 124.68, 122.21, 60.68, 39.87, 29.83, 21.27, 14.40. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>23</sub>NO<sub>2</sub> 356.1771; Found 356.1779.

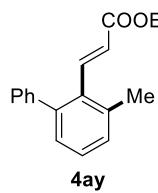
**ethyl (E)-3-((3,5-dimethylisoxazol-4-yl)methyl)-[1,1'-biphenyl]-2-yl)acrylate (4ax)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 25:1) afforded **4ax** as a white solid. 41% yield (14.8 mg). m.p. 74-75 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 16.4 Hz, 1H), 7.38 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.34-7.31 (m, 1H), 7.30-7.22 (m, 4H), 7.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.72 (d, *J* = 16.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 2H), 2.25 (s, 3H), 2.06 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.35, 165.96, 160.15, 142.77, 142.67, 141.00, 137.33, 133.07, 129.85, 129.25, 128.68, 128.34, 127.92, 127.43, 125.46, 111.68, 60.65, 26.90, 14.33, 11.19, 10.53. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>23</sub>NO<sub>3</sub> 356.1771; Found 356.1779.

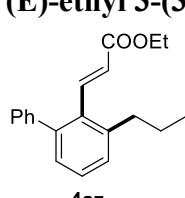
**ethyl (E)-3-(3-methyl-[1,1'-biphenyl]-2-yl)acrylate (4ay)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4ay** as a white solid. 42% yield (11.2 mg).

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 16.4 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.27 (dd, *J* = 7.6, 2.0 Hz, 3H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.18 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.81 (d, *J* = 16.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.80, 143.59, 142.68, 141.33, 137.23, 132.86, 130.07, 129.89, 128.50, 128.44, 128.25, 127.30, 124.33, 60.45, 21.66, 14.35. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> 266.1301; Found 266.1310.

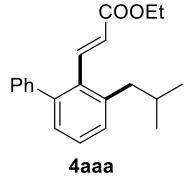
**(E)-ethyl 3-(3-propyl-[1,1'-biphenyl]-2-yl)acrylate (4az)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4az** as a white solid. 40% yield (11.8 mg). m.p. 59-60 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 16.4 Hz, 1H), 7.38-7.34 (m, 2H), 7.33-7.29 (m, 2H), 7.28-7.23 (m, 3H), 7.18 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.65 (d, *J* = 16.3 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.75-2.68 (m, 2H), 1.66-1.63 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.70, 143.38, 142.34, 141.92, 141.65, 132.74, 129.92, 128.94, 128.51, 128.43, 128.25, 127.16, 124.77, 60.43, 36.11, 24.52, 14.35, 14.23. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub> 294.1614; Found 294.1606.

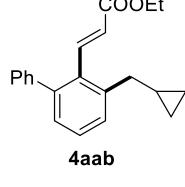
**ethyl (E)-3-(3-isobutyl-[1,1'-biphenyl]-2-yl)acrylate (4aaa)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **4aaa** as a white solid. 34% yield (10.0 mg). m.p. 60-61 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 16.4 Hz, 1H), 7.35 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.32-7.24 (m, 4H), 7.22-7.15 (m, 2H), 5.59 (d, *J* = 16.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.62 (d, *J* = 7.2 Hz, 2H), 1.87 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.67, 143.50, 142.25, 141.73, 141.06, 133.00, 129.88, 129.79, 128.63, 128.25, 128.15, 127.11, 124.91, 60.40, 43.19, 29.94, 22.63, 14.34. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub> 294.1614; Found 294.1606.

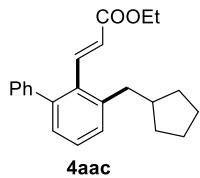
**ethyl (E)-3-(3-(cyclopropylmethyl)-[1,1'-biphenyl]-2-yl)acrylate (4aab)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4aab** as a white solid. 43% yield (13.1 mg). m.p. 61-61 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 16.4 Hz, 1H), 7.46-7.42 (m, 1H), 7.39-7.24 (m, 6H), 7.20 (d, *J* = 7.5 Hz, 1H), 5.68 (d, *J* = 16.3 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.69 (d, *J* = 6.7 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.04-0.96 (m, 1H), 0.59-0.54 (m, 2H), 0.26-0.21 (m, 2H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.68, 143.44, 142.24, 141.57, 141.21, 132.76, 129.91, 128.64, 128.50, 128.48, 128.24, 127.17, 124.91, 60.45, 38.25, 14.34, 11.41, 5.09. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub> 294.1614; Found 294.1606.

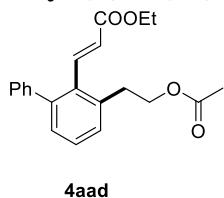
**ethyl (E)-3-(3-(cyclopentylmethyl)-[1,1'-biphenyl]-2-yl)acrylate (4aac)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **4aac** as a white solid. 40% yield (13.4 mg). m.p. 57-58 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 16.3 Hz, 1H), 7.35 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.32-7.24 (m, 4H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.17 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.62 (d, *J* = 16.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.76 (d, *J* = 7.3 Hz, 2H), 2.14-2.03 (m, 1H), 1.72 (dd, *J* = 11.7, 7.0 Hz, 2H), 1.65 (dd, *J* = 9.4, 5.2 Hz, 2H), 1.57-1.47 (m, 2H), 1.25-1.17 (m, 5H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.71, 143.52, 142.24, 141.73, 141.63, 132.76, 129.88, 129.31, 128.50, 128.26, 128.23, 127.10, 124.86, 60.40, 41.54, 39.80, 32.68, 24.94, 14.33. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>26</sub>O<sub>2</sub> 294.1614; Found 294.1606.

**ethyl (E)-3-(3-(2-acetoxyethyl)-[1,1'-biphenyl]-2-yl)acrylate (4aad)**

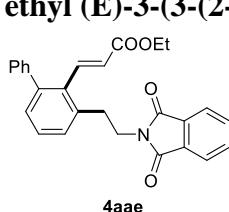


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 25:1) afforded **4aad** as a white solid. 39% yield (13.2 mg). m.p. 59-60 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 16.3 Hz, 1H), 7.39-7.30 (m, 4H), 7.28-7.23 (m, 4H), 5.71 (d, *J* = 16.3 Hz, 1H), 4.28 (t, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.09 (t, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 171.12, 166.42, 142.91, 142.52, 141.26, 136.79, 133.53, 129.88, 129.35, 128.62, 128.48, 128.31, 127.33, 125.54, 64.56, 60.56, 32.89, 21.10, 14.34.

**HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>22</sub>O<sub>4</sub> 294.1614; Found 294.1606.

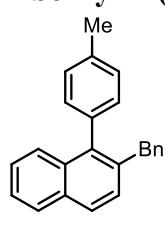
**ethyl (E)-3-(3-(2-(1,3-dioxoisoxindolin-2-yl)ethyl)-[1,1'-biphenyl]-2-yl)acrylate (4aae)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 15:1) afforded **4aae** as a white solid. 35% yield (14.8 mg). m.p. 81-82 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.86-7.76 (m, 3H), 7.73-7.67 (m, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.32-7.24 (m, 5H), 7.21 (dd, *J* = 6.5, 2.3 Hz, 1H), 5.75 (d, *J* = 16.3 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.97-3.88 (m, 2H), 3.18-3.08 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 168.13, 166.35, 142.47, 141.26, 137.06, 134.21, 134.01, 133.51, 132.19, 129.83, 129.42, 129.34, 128.62, 128.26, 127.24, 125.71, 123.36, 60.50, 38.60, 32.71, 14.32. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>23</sub>NO<sub>4</sub> 294.1614; Found 294.1606.

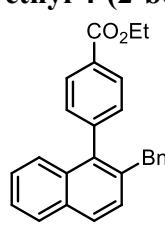
**2-benzyl-1-(p-tolyl)naphthalene (5a)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5a** as a white solid. 61% yield (18.8 mg). m.p. 105-107 °C.

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.47-7.38 (m, 2H), 7.37-7.29 (m, 2H), 7.27-7.12 (m, 7H), 7.01 (d, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 2.44 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.72, 138.67, 136.83, 136.19, 136.09, 133.31, 132.22, 130.36, 129.12, 129.03, 128.33, 128.28, 127.85, 127.60, 126.83, 125.94, 125.88, 125.25, 39.57, 21.46. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>20</sub> 308.1560; Found 305.1558.

**ethyl 4-(2-benzylnaphthalen-1-yl)benzoate (5b)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **5b** as a white solid. 68% yield (24.9 mg). m.p. 113-114 °C.

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.47-7.37 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.11-7.22 (m, 3H), 6.96 (d, *J* = 7.0 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.72, 144.36, 141.21, 137.63, 135.80, 132.71, 132.21, 130.65, 129.68, 129.55, 128.89, 128.41, 128.36, 128.20, 128.00, 126.33, 126.28, 126.05, 125.51, 61.20, 39.60, 14.53. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>2</sub> 366.1614; Found 366.1612.

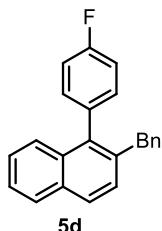
### **2-benzyl-1-(4-chlorophenyl)naphthalene (5c)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5c** as a white solid. 70% yield (23.0 mg). m.p. 140-141 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 (m, 2H), 7.47-7.32 (m, 6H), 7.17 (m, 5H), 6.97 (d, *J* = 7.3 Hz, 2H), 3.91 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 141.35, 137.77, 137.40, 136.13, 133.38, 133.07, 132.32, 131.91, 128.92, 128.69, 128.42, 128.40, 128.10, 128.00, 126.40, 126.25, 126.05, 125.47, 77.48, 77.16, 76.84, 39.70. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>17</sub>Cl 328.1013; Found 328.1024.

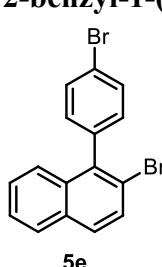
### **2-benzyl-1-(4-fluorophenyl)naphthalene (5d)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5d** as a white solid. 62% yield (19.3 mg). m.p. 115-116 °C

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 (m, 2H), 7.47-7.41 (m, 1H), 7.41-7.32 (m, 3H), 7.22-7.16 (m, 4H), 7.14 (t, *J* = 8.7 Hz, 3H), 6.97 (d, *J* = 7.1 Hz, 2H), 3.91 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 162.22 (d, *J* = 246.0 Hz), 141.42, 137.60, 136.30, 135.05 (d, *J* = 3.5 Hz), 133.27, 132.27, 132.09, 132.03, 128.90, 128.41, 128.38, 127.97, 126.32 (d, *J* = 34.8 Hz), 126.00, 125.41, 115.48, 115.31, 39.70. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -115.36. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>17</sub>F 312.1309; Found 312.1310.

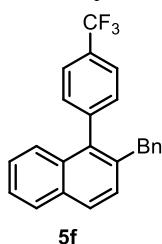
### **2-benzyl-1-(4-bromophenyl)naphthalene (5e)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5e** as a white solid. 63% yield (23.5 mg). m.p. 145-146 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.47-7.42 (m, 1H), 7.40-7.35 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.09-7.17 (m, 3H), 6.97 (d, *J* = 6.9 Hz, 2H), 3.91 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 141.33, 138.27, 137.37, 136.06, 132.99, 132.31, 132.27, 131.64, 128.92, 128.43, 128.40, 128.13, 128.00, 126.40, 126.27, 126.05, 125.49, 121.53, 77.48, 77.16, 76.84, 39.70. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>17</sub>Br 372.0508; Found 372.0499.

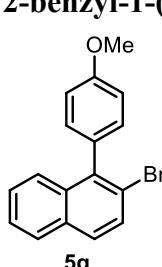
### **2-benzyl-1-(4-(trifluoromethyl)phenyl)naphthalene (5f)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5f** as a white solid. 63% yield (22.8 mg). m.p. 124-125 °C

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.86 (m, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.38-7.33 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.23-7.11 (m, 3H), 6.95 (d, *J* = 7.1 Hz, 2H), 3.89 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.33, 141.16, 137.22, 136.03, 132.80, 130.97, 129.84, 129.52, 128.90, 128.45, 128.43, 128.37, 128.07, 126.41, 126.22, 126.12, 125.79, 125.59, 125.47, 125.43, 125.40, 125.36, 123.09, 77.48, 77.16, 76.84, 39.72. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.36. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub> 362.1277; Found 362.1269.

### **2-benzyl-1-(4-methoxyphenyl)naphthalene (5g)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5g** as a white solid. 55% yield (17.8 mg). m.p. 165-166 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.48-7.39 (m, 2H), 7.39-7.31 (m, 2H), 7.23-7.11 (m, 5H), 7.03-6.96 (m, 4H), 3.94 (s, 2H), 3.88 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 158.80, 141.73, 138.38, 136.38, 133.55, 132.28, 131.55, 131.41, 129.00, 128.34, 127.87, 127.62, 126.80, 125.97, 125.89, 125.27, 113.81, 55.43, 39.65. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>20</sub>O 324.1509; Found 324.1511.

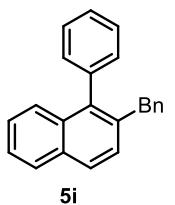
**(4-(2-benzylnaphthalen-1-yl)phenyl)trimethylsilane (5h)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 150:1) afforded **5h** as a white solid. 76% yield (27.8 mg). m.p. 124-125 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.47-7.39 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 (s, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 0.33 (s, 9H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.71, 139.68, 139.16, 138.69, 136.05, 133.38, 133.11, 132.21, 129.78, 129.09, 128.34, 128.28, 127.85, 127.71, 126.86, 126.01, 125.91, 125.32, 39.59, -0.85. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>26</sub>Si 366.1798; Found 366.1796.

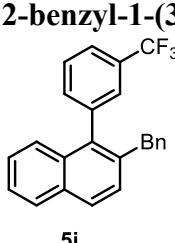
**2-benzyl-1-phenylnaphthalene (5i)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5i** as a white solid. 55% yield (16.2 mg). m.p. 75-76 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.48-7.31 (m, 7H), 7.27-7.25 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.0 Hz, 2H), 3.92 (s, 2H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.62, 139.29, 138.66, 136.02, 133.17, 132.22, 130.51, 129.02, 128.42, 128.34, 128.32, 127.87, 127.75, 127.30, 126.75, 126.03, 125.92, 125.32, 39.62. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>18</sub> 294.1403; Found 294.1400.

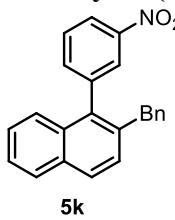
**2-benzyl-1-(3-(trifluoromethyl)phenyl)naphthalene (5j)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5j** as a white solid. 67% yield (24.2 mg). m.p. 57-59 °C

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.86 (t, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.48-7.40 (m, 4H), 7.39-7.33 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.21-7.11 (m, 3H), 6.92 (d, *J* = 7.0 Hz, 2H), 3.89 (s, 2H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.07, 140.10, 137.04, 136.31, 133.88, 132.89, 132.29, 130.8 (q, *J* = 31.3 Hz), 128.95, 128.82, 128.48, 128.43, 128.37, 128.07, 127.3 (q, *J* = 3.7 Hz), 126.43, 126.14, 126.10, 125.56, 124.26 (q, *J* = 3.7 Hz), 124.23 (q, *J* = 271.3 Hz), 39.87. **19F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.48. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub> 362.1277; Found 362.1288.

**2-benzyl-1-(3-nitrophenyl)naphthalene (5k)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 90:1) afforded **5k** as a white solid. 48% yield (16.3 mg). m.p. 66-67 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.28 (ddd, *J* = 8.2, 2.4, 1.2 Hz, 1H), 8.10-8.05 (m, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.54 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.50-7.41 (m, 2H), 7.37 (t, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 5.0 Hz, 1H), 7.20-7.11 (m, 3H), 6.94-6.87 (m, 2H), 3.90 (s, 2H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 148.30, 141.08, 140.81, 136.76, 136.35, 136.02, 132.67, 132.32, 129.44, 128.77, 128.52, 128.48, 128.20, 126.65, 126.23, 125.78, 125.73, 125.55, 122.50, 39.90. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>17</sub>NO<sub>2</sub> 339.1254; Found 339.1245.

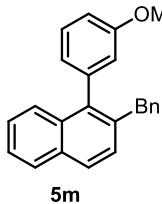
**2-benzyl-1-(3-(tert-butyl)phenyl)naphthalene (5l)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5l** as a white solid. 60% yield (21.0 mg). m.p. 124-126 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.45-7.33 (m, 6H), 7.22 (t, *J* = 1.6 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.13-7.08 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 3.93 (s, 2H), 1.26 (s, 9H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 151.13, 141.76, 139.30, 138.73, 135.93, 133.26, 132.28, 128.89, 128.50, 128.31, 127.98, 127.86, 127.77, 127.59, 127.41, 126.86, 125.98, 125.85, 125.27, 124.06, 39.74, 34.80, 31.44. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>26</sub> 350.2029; Found 350.2022.

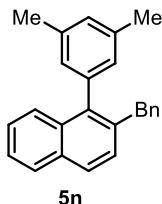
## **2-benzyl-1-(3-methoxyphenyl)naphthalene (5m)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5m** as a white solid. 56% yield (18.2 mg). m.p. 82-83 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.82 (m, 2H), 7.47-7.31 (m, 5H), 7.40-7.32 (m, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.04-6.98 (m, 2H), 6.96 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.76-6.72 (m, 1H), 3.98-3.89 (m, 2H), 3.71 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 159.50, 141.71, 140.64, 138.55, 135.87, 133.05, 132.20, 129.44, 128.99, 128.37, 128.33, 127.84, 127.75, 126.75, 126.06, 125.90, 125.35, 122.84, 115.60, 113.28, 55.25, 39.67. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>20</sub>O 324.1509; Found 324.1511.

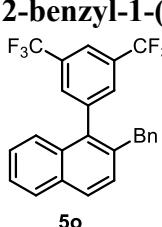
## **2-benzyl-1-(3,5-dimethylphenyl)naphthalene (5n)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5n** as a white solid. 51% yield (16.4 mg). m.p. 79-80 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.38-7.46 (m, 2H), 7.31-7.37 (m, 2H), 7.24-7.16 (m, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 5.1 Hz, 2H), 6.84 (s, 2H), 3.91 (s, 2H), 2.33 (s, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.83, 139.06, 138.99, 137.72, 135.98, 133.20, 132.19, 129.09, 128.79, 128.30, 128.26, 127.80, 127.45, 126.89, 125.87, 125.84, 125.21, 39.77, 21.52. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>22</sub> 322.1716; Found 322.1721.

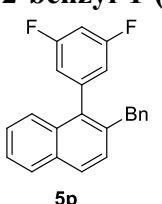
## **2-benzyl-1-(3,5-bis(trifluoromethyl)phenyl)naphthalene (5o)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5o** as a white solid. 55% yield (23.7 mg). m.p. 73-74 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.96-7.86 (m, 3H), 7.61 (s, 2H), 7.52-7.45 (m, 2H), 7.39 (t, *J* = 8.3 Hz, 1H), 7.21-7.10 (m, 4H), 6.84 (d, *J* = 8.1 Hz, 2H), 3.88 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.49, 140.55, 136.63, 135.44, 132.61, 132.37, 131.7 (q, *J* = 33.7 Hz), 130.77, 129.01, 128.71, 128.60, 128.52, 128.28, 126.87, 126.31, 125.83, 125.48, 123.4 (q, *J* = 271.3 Hz), 121.4 (q, *J* = 3.7 Hz), 40.21. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.72. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>16</sub>F<sub>6</sub> 430.1151; Found 430.1156.

## **2-benzyl-1-(3,5-difluorophenyl)naphthalene (5p)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5p** as a white solid. 54% yield (17.8 mg). m.p. 55-56 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.89-7.78 (m, 2H), 7.48-7.43 (m, 1H), 7.41-7.34 (m, 3H), 7.24-7.19 (m, 2H), 7.19-7.13 (m, 1H), 6.98 (d, *J* = 6.9 Hz, 2H), 6.88 (tt, *J* = 9.1, 2.4 Hz, 1H), 6.81-6.73 (m, 2H), 3.92 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 163.05 (dd, *J* = 249.7, 13.0 Hz), 142.80 (t, *J* = 9.3 Hz), 141.01, 136.25, 136.02, 132.54, 132.25, 128.90, 128.52, 128.50, 128.32, 128.07, 126.52, 126.21, 126.02, 125.66, 113.68 (dd, *J* = 18.7, 6.3 Hz), 102.99 (t, *J* = 25.0 Hz), 39.67. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -109.85. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>16</sub>F<sub>2</sub> 330.1215; Found 330.1219.

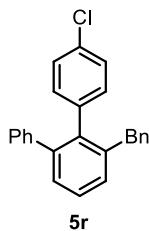
## **2-benzyl-1-(4-chlorophenyl)-4-methylnaphthalene (5q)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5q** as a white solid. 60% yield (20.6 mg). m.p. 97-98 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.51-7.46 (m, 1H), 7.43-7.33 (m, 4H), 7.25-7.13 (m, 6H), 6.98 (d, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 2.69 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.42, 137.94, 135.76, 135.63, 134.33, 133.19, 133.13, 132.10, 131.46, 129.09, 128.88, 128.61, 128.38, 127.00, 125.98, 125.91, 125.32, 124.19, 39.58, 19.68. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>19</sub>Cl 342.1170; Found 342.1168.

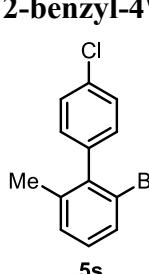
### 3'-benzyl-4''-chloro-1,1':2',1''-terphenyl (5r)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5r** as a white solid. 40% yield (14.2 mg). m.p. 111-112 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.27-7.24 (m, 1H), 7.23-7.18 (m, 2H), 7.17-7.09 (m, 6H), 7.03 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 142.13, 141.74, 141.19, 139.47, 139.42, 138.36, 132.52, 132.06, 129.91, 129.54, 128.96, 128.46, 128.38, 127.96, 127.78, 127.73, 126.40, 126.00, 77.48, 77.16, 76.84, 39.93. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>19</sub>Cl 354.1170; Found 354.1177.

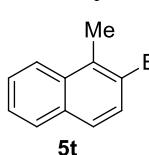
### 2-benzyl-4'-chloro-6-methyl-1,1'-biphenyl (5s)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 100:1) afforded **5s** as a white solid. 56% yield (16.4 mg). m.p. 69-70 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.24-7.06 (m, 6H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.2 Hz, 2H), 3.70 (s, 2H), 2.00 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.19, 140.72, 139.01, 138.91, 136.56, 132.77, 130.82, 128.89, 128.60, 128.26, 128.24, 128.06, 127.73, 127.65, 125.87, 39.84, 21.11. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>Cl 292.1013; Found 292.1015.

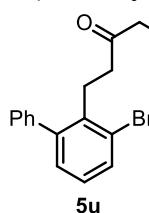
### 2-benzyl-1-methylnaphthalene (5t)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 200:1) afforded **5t** as a white solid. 36% yield (8.4 mg). m.p. 69-70 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.52-7.41 (m, 2H), 7.33-7.22 (m, 3H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 4.22 (s, 2H), 2.59 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 141.05, 135.67, 133.23, 132.64, 131.91, 129.20, 128.68, 128.59, 128.55, 126.27, 126.03, 126.00, 125.08, 124.18, 40.16, 14.85. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>16</sub> 232.1247; Found 232.1250.

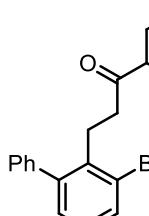
### 1-(3-benzyl-[1,1'-biphenyl]-2-yl)pentan-3-one (5u)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **5u** as a white solid. 63% yield (20.7 mg). m.p. 81-82 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40-7.35 (m, 2H), 7.34-7.30 (m, 1H), 7.29-7.26 (m, 4H), 7.22-7.14 (m, 5H), 7.09 (dd, *J* = 7.0, 1.9 Hz, 1H), 4.07 (s, 2H), 2.88-2.80 (m, 2H), 2.05-1.96 (m, 4H), 0.83 (t, *J* = 7.3 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 210.71, 143.26, 142.16, 141.01, 139.11, 137.49, 130.36, 129.18, 128.94, 128.90, 128.59, 128.24, 127.06, 126.19, 125.97, 42.34, 39.93, 35.47, 23.74, 7.80. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>24</sub>O 328.1822; Found 328.1829.

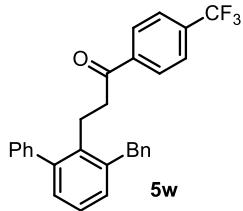
### 3-(3-benzyl-[1,1'-biphenyl]-2-yl)-1-cyclohexylpropan-1-one (5v)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **5v** as a white solid. 65% yield (24.8 mg). m.p. 91-92 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40-7.34 (m, 2H), 7.34-7.29 (m, 1H), 7.29-7.24 (m, 4H), 7.23-7.13 (m, 5H), 7.11-7.07 (m, 1H), 4.07 (s, 2H), 2.89-2.83 (m, 2H), 2.14-2.02 (m, 2H), 1.93-1.82 (m, 1H), 1.68-1.54 (m, 3H), 1.51-1.38 (m, 2H), 1.16-0.94 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 213.15, 143.28, 142.25, 141.05, 139.09, 137.67, 130.33, 129.22, 128.92, 128.85, 128.60, 128.23, 127.03, 126.17, 125.94, 50.50, 40.65, 39.81, 28.34, 25.90, 25.69, 23.90. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>30</sub>O 382.2291; Found 382.2280.

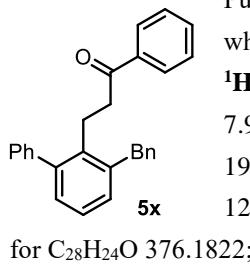
### 3-(3-benzyl-[1,1'-biphenyl]-2-yl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (5w)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **5w** as a white solid. 50% yield (22.2 mg). m.p. 121-122 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.53 (q, *J* = 8.5 Hz, 4H), 7.43-7.30 (m, 5H), 7.27-7.25 (m, 2H), 7.24-7.20 (m, 2H), 7.17 (d, *J* = 7.0 Hz, 2H), 7.13 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 4.13 (s, 2H), 3.05-2.97 (m, 2H), 2.60-2.53 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 198.46, 143.36, 142.21, 140.94, 139.25, 139.11, 134.22 (q, *J* = 32.0 Hz), 133.73, 130.60, 129.31, 129.06, 128.91, 128.67, 128.49, 128.39, 127.19, 126.30, 126.27, 125.57 (q, *J* = 4.0 Hz), 123.72 (q, *J* = 271.0 Hz), 40.00, 39.41, 24.64. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -63.08. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>23</sub>F<sub>3</sub>O 444.1696; Found 444.1694.

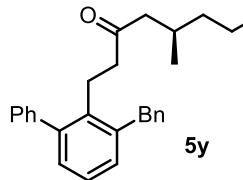
### 3-(3-benzyl-[1,1'-biphenyl]-2-yl)-1-phenylpropan-1-one (**5x**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **5x** as a white solid. 52% yield (19.6 mg). m.p. 81-82 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.52-7.43 (m, 3H), 7.41-7.28 (m, 7H), 7.26-7.15 (m, 6H), 7.11 (t, *J* = 7.9 Hz, 2H), 4.12 (s, 2H), 3.08-2.97 (m, 2H), 2.70-2.58 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.44, 143.34, 142.25, 140.90, 139.30, 137.42, 136.46, 132.94, 130.41, 129.30, 128.94, 128.62, 128.52, 128.41, 128.08, 127.11, 126.21, 126.12, 39.81, 39.24, 24.78. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>24</sub>O 376.1822; Found 376.1815.

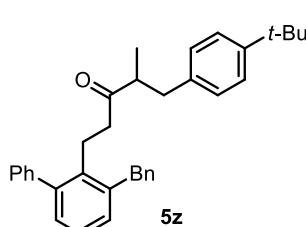
### (R)-1-(3-benzyl-[1,1'-biphenyl]-2-yl)-5,9-dimethyldec-8-en-3-one (**5y**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 60:1) afforded **5y** as a white solid. 61% yield (25.9 mg). m.p. 85-86 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.37 (t, *J* = 7.3 Hz, 2H), 7.33-7.26 (m, 5H), 7.19 (m, 5H), 7.09 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.06-4.99 (m, 1H), 4.07 (s, 2H), 2.90-2.82 (m, 2H), 2.07-1.95 (m, 3H), 1.92-1.69 (m, 4H), 1.67 (s, 3H), 1.57 (s, 3H), 1.15-0.98 (m, 2H), 0.68 (d, *J* = 6.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 210.11, 143.29, 142.21, 141.02, 139.12, 137.48, 131.53, 130.33, 129.20, 128.93, 128.88, 128.63, 128.26, 127.07, 126.20, 125.99, 124.47, 49.85, 43.39, 39.85, 37.05, 29.11, 25.84, 25.53, 23.72, 19.70, 17.78. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>36</sub>O 424.2761; Found 424.2751.

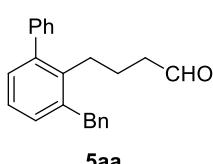
### 5-(3-benzyl-[1,1'-biphenyl]-2-yl)-1-(4-(tert-butyl)phenyl)-2-methylpentan-3-one (**5z**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **5z** as a white solid. 51% yield (24.2 mg). m.p. 97-98 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.36 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.28-7.13 (m, 11H), 7.08 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.02 (s, 2H), 2.85-2.75 (m, 2H), 2.66 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.38 (dt, *J* = 8.1, 6.7 Hz, 1H), 2.25 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.17-1.97 (m, 2H), 1.29 (s, 9H), 0.76 (d, *J* = 6.9 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 213.02, 149.03, 143.28, 142.22, 141.03, 139.16, 137.50, 136.66, 130.32, 129.19, 128.92, 128.87, 128.66, 128.61, 128.25, 127.07, 126.20, 125.98, 125.32, 47.83, 41.50, 39.83, 38.22, 34.48, 31.52, 23.65, 16.16. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>38</sub>O 474.2917; Found 474.2902.

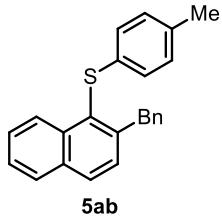
### 4-(3-benzyl-[1,1'-biphenyl]-2-yl)butanal (**5aa**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **5aa** as a white solid. 38% yield (11.9 mg). m.p. 57-58 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.37 (t, *J* = 1.8 Hz, 1H), 7.42-7.36 (m, 2H), 7.36-7.32 (m, 1H), 7.31-7.27 (m, 4H), 7.22-7.16 (m, 4H), 7.15-7.12 (m, 1H), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.12 (s, 2H), 2.63-2.53 (m, 2H), 2.12 (td, *J* = 7.1, 1.8 Hz, 2H), 1.55-1.47 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 202.48, 143.21, 142.47, 141.11, 139.06, 137.86, 130.27, 129.35, 128.91, 128.83, 128.61, 128.18, 127.00, 126.23, 125.99, 43.73, 39.50, 29.10, 23.00. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>22</sub>O 314.1665; Found 314.1652.

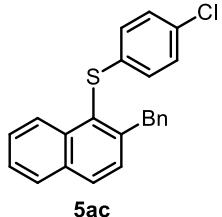
### (2-benzylnaphthalen-1-yl)(p-tolyl)sulfane (**5ab**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **5ab** as a white solid. 67% yield (22.8 mg). m.p. 82-83 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.54 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, 6.9, 1.4 Hz, 1H), 7.52-7.43 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.25-7.21 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 4.49 (s, 2H), 2.23 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 145.33, 140.94, 135.69, 134.94, 134.76, 133.25, 130.38, 129.80, 129.19, 128.61, 128.52, 128.44, 127.88, 127.46, 127.04, 126.41, 126.14, 125.93, 41.12, 20.99. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>20</sub>S 340.1280; Found 340.1266.

### (2-benzylnaphthalen-1-yl)(4-chlorophenyl)sulfane (**5ac**)

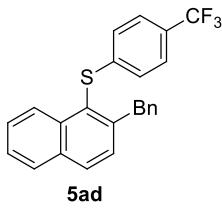


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **5ac** as a white solid. 34% yield (12.3 mg). m.p. 68-69 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.46 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.87-7.83 (m, 1H), 7.54-7.47 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.19-7.12 (m, 3H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.47 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 145.55, 140.60, 137.07, 135.43, 133.29, 130.83, 130.68, 129.11, 129.06, 128.72, 128.58, 128.56, 127.71, 127.35, 126.86, 126.66, 126.23, 126.13, 41.18. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>17</sub>ClS 360.0734;

Found 360.0738.

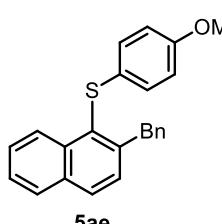
### (2-benzylnaphthalen-1-yl)(4-(trifluoromethyl)phenyl)sulfane (**5ad**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 90:1) afforded **5ad** as a white solid. 30% yield (11.8 mg). m.p. 72-73 °C

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.45-8.40 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.89-7.85 (m, 1H), 7.54-7.46 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.16-7.11 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 2H), 4.46 (s, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 145.87, 143.66, 140.40, 135.51, 133.36, 131.16, 129.12, 128.89 (q, *J* = 26.3 Hz), 128.83, 128.68, 128.57, 127.91, 126.47, 126.30, 126.27, 125.79, 125.75, 125.72, 124.65 (q, *J* = 253.7 Hz), 41.26. **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -62.34. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>17</sub>F<sub>3</sub>S 394.0998; Found 394.0995.

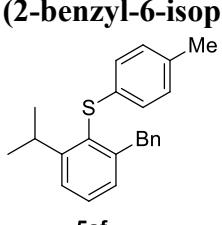
### (2-benzylnaphthalen-1-yl)(4-methoxyphenyl)sulfane (**5ae**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **5ae** as a white solid. 31% yield (11.1 mg). m.p. 96-97 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.58 (d, *J* = 8.4 Hz, 1H), 7.86-7.79 (m, 2H), 7.53-7.43 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.19-7.11 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.51 (s, 2H), 3.71 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 157.73, 145.04, 140.97, 135.64, 133.28, 130.24, 129.19, 128.78, 128.63, 128.52, 128.44, 128.41, 127.40, 127.08, 126.14, 125.90, 114.78, 55.43, 41.15. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>20</sub>OS 356.1229; Found 356.1210.

### (2-benzyl-6-isopropylphenyl)(p-tolyl)sulfane (**5af**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 80:1) afforded **5af** as a white solid. 51% yield (16.9 mg). m.p. 74-75 °C.

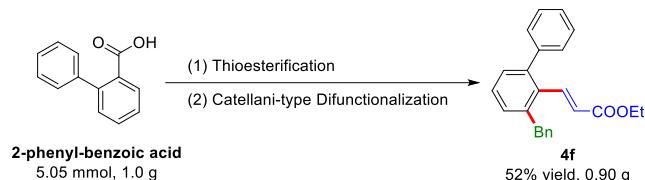
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.33 (t, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 7.04 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 4.18 (s, 2H), 3.74 (hept, *J* = 6.9 Hz, 1H), 2.26 (s, 3H), 1.15 (d, *J* = 6.9 Hz, 6H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 154.42, 146.62, 141.04, 135.56, 134.44, 129.94, 129.76, 129.72, 129.33, 128.43, 128.39, 125.97, 125.79, 124.68, 40.94, 31.63, 24.25, 21.01. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>24</sub>S 332.1593; Found 332.1594.

### (2-benzyl-6-methylphenyl)(ethyl)sulfane (**5ag**)



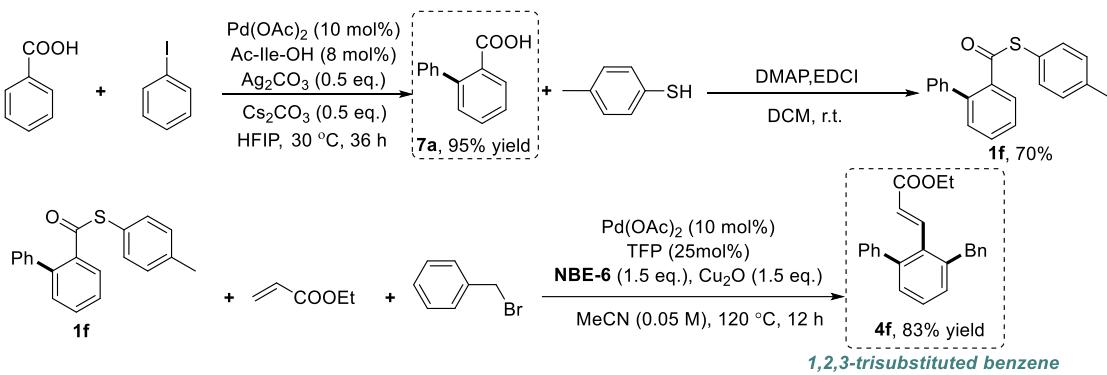
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 70:1) afforded **5ag** as a white solid. 40% yield (9.7 mg). m.p. 62–63 °C.  
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.28–7.24 (m, 2H), 7.21–7.11 (m, 5H), 7.04 (dd, *J* = 5.4, 3.7 Hz, 1H), 4.35 (s, 2H), 2.60–2.51 (m, 5H), 1.13 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 145.96, 143.75, 141.70, 133.89, 129.11, 128.72, 128.42, 128.36, 125.94, 41.02, 29.92, 22.23, 14.75. **HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>18</sub>S 242.1124; Found 242.1124.

## 5. Procedures for the gram-scale one-pot synthesis:



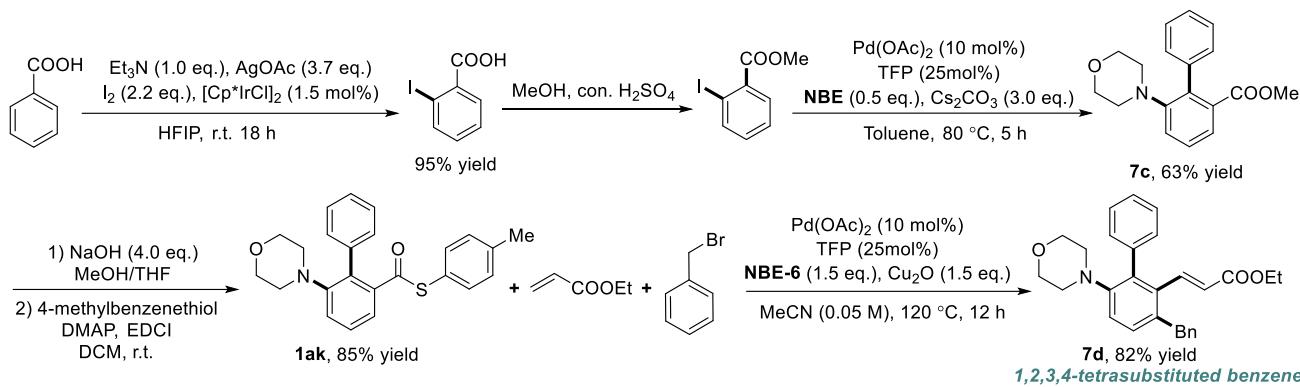
An oven dried 100 mL Schlenk tube was charged with 2-phenyl-benzoic acid (1.0g, 5.05 mmol, 1.0 equiv), DCC (1.15 g, 5.55 mmol, 1.1 equiv), DMAP (13 mg, 0.1 mmol, 0.02 equiv), 3 mL anhydrous DCE and 15 mL MeCN. The mixture was stirred for 10 min at room temperature. After that, 4-methylbenzenethiol (627.2 mg, 5.30 mmol, 1.05 equiv) was added to the mixture directly. The reaction mixture was stirred at room temperature for another 6 h. Then, Pd(OAc)<sub>2</sub> (112 mg, 0.5 mmol, 0.1 eq.), TFP (293 mg, 1.26 mmol, 0.25 eq.), **NBE-6** (1.92 g, 7.56 mmol, 1.5 eq.), Cu<sub>2</sub>O (1.08 g, 7.56 mmol, 1.5 eq.), ethyl acrylate (0.83 mL, 7.56 mmol, 1.5 eq.), benzyl bromide (2.59 g, 15.15 mmol, 3.0 eq.) were added to the same vessel. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for 12 h under N<sub>2</sub> atmosphere. Then the reaction mixture was cooled to room temperature, EtOAc (5 mL) and ammonium hydroxide (3 mL) were added, and the resulting mixture was continuously stirred at room temperature for another 30 min. The mixture was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/Hexane) to afford the products **4f** in 52% yield.

## 6. Access to polysubstituted benzenes from benzoic acid



**Scheme S2.** Trisubstituted benzenes from benzoic acid

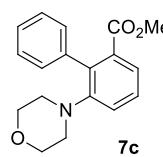
*ortho*-Phenylation of benzoic acid was synthesized according to literature.<sup>1</sup> Thioester **1f** and the desired product **4f** were prepared following the general procedures described above.



**Scheme S3.** Tetrasubstituted benzenes from benzoic acid

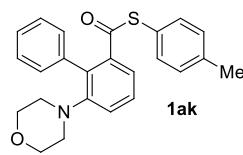
2-iodobenzoic acid<sup>2</sup> and compound 7c<sup>3</sup> was synthesized according to literature. Thioester **1ak** and the desired product **7d** were prepared following the general procedures described above.

### methyl 6-morpholino-[1,1'-biphenyl]-2-carboxylate (**7c**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **7c** as a white solid. Known compound. 63% yield (1.87 g, *two steps from 10 mmol 2-iodobenzoic acid*).  
**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.43-7.33 (m, 6H), 7.32-7.27 (m, 1H), 7.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.52 (s, 3H), 3.49-3.44 (m, 4H), 2.76-2.71 (m, 4H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 169.72, 151.07, 138.49, 135.68, 134.14, 129.56, 128.39, 127.96, 127.16, 123.55, 121.86, 67.00, 52.03, 51.79.

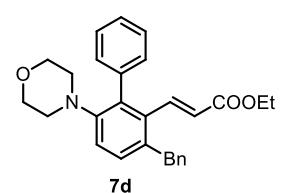
### S-p-tolyl 6-morpholino-[1,1'-biphenyl]-2-carbothioate (**1ak**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 10:1) afforded **1ak** as a white solid. 85% yield (661 mg, *from 2 mmol 7c*); m.p. 154-155 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.48-7.43 (m, 2H), 7.38 (td, *J* = 7.6, 2.4 Hz, 3H), 7.34-7.28 (m, 2H), 7.19-7.12 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.52-3.45 (m, 4H), 2.80-2.74 (m, 4H), 2.36-2.33 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 194.45, 151.00, 141.24, 139.70, 137.35, 134.47, 133.33, 130.41, 130.07, 128.48, 128.08, 127.54, 124.48, 121.55, 121.36, 66.95, 51.66, 21.45. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>23</sub>NO<sub>2</sub>S 389.1444; Found 389.1435.

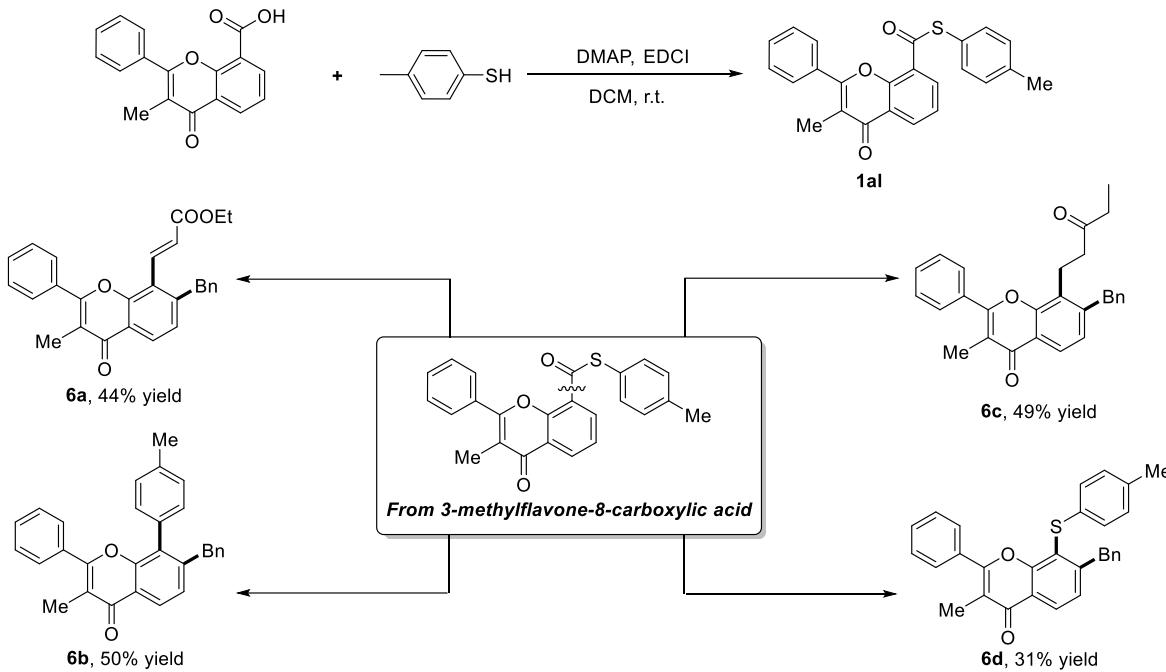
### (E)-ethyl 3-(3-benzyl-6-morpholino-[1,1'-biphenyl]-2-yl)acrylate (**7d**)



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 30:1) afforded **7d** as a white solid. 82% yield (35.0 mg). m.p. 111-112 °C.

**1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 16.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29-7.23 (m, 5H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16-7.09 (m, 3H), 7.00 (d, *J* = 8.3 Hz, 1H), 5.55 (d, *J* = 16.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 3.47-3.39 (m, 4H), 2.75-2.69 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.40, 149.26, 144.14, 140.86, 138.29, 136.37, 135.35, 134.00, 131.16, 130.58, 129.09, 128.61, 127.99, 127.09, 126.22, 124.61, 119.32, 67.09, 60.36, 51.87, 39.62, 14.33. **HRMS** (EI-ESA) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>29</sub>NO<sub>3</sub> 427.2142; Found 427.2139.

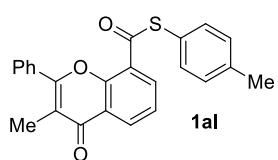
## 7. Two-step functionalization of 3-methylflavone-8-carboxylic acid



**Scheme S4.** Two-step functionalization of 3-methylflavone-8-carboxylic acid

Thioester **1al** and the desired product **6a-6d** were prepared following the general procedures described above.

### **S-p-tolyl 3-methyl-4-oxo-2-phenyl-4H-chromene-8-carbothioate (1al)**

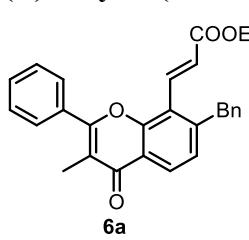


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 8:1) afforded **1al** as a white solid. 39% yield (1.50 g); m.p. 134–135 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.46 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.21 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.83–7.71 (m, 2H), 7.54–7.45 (m, 4H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.24 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 188.23, 178.15, 161.23, 152.92, 140.26, 134.89, 133.75, 132.76, 130.65, 130.59, 130.33, 129.60, 128.52, 127.59, 124.32, 123.88, 123.29, 118.08, 21.53, 11.98.

**HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>3</sub>S 386.0971; Found 386.0972.

### **(E)-ethyl 3-(7-benzyl-3-methyl-4-oxo-2-phenyl-4H-chromen-8-yl)acrylate (6a)**

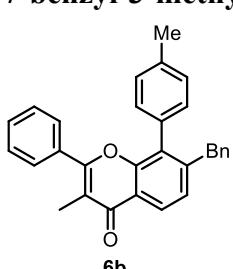


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 30:1) afforded **6a** as a white solid. 44% yield (18.7 mg). m.p. 121–122 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 16.3 Hz, 1H), 7.66 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.57–7.49 (m, 3H), 7.32–7.27 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.61 (d, *J* = 16.3 Hz, 1H), 4.28–4.18 (m, 4H), 2.21 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 178.68, 166.87, 160.99, 154.71, 146.61, 139.17, 136.23, 133.17, 130.55, 129.22, 128.88, 128.67, 127.50, 126.81, 126.74, 125.66, 123.21, 121.52, 117.81, 60.70, 40.00, 14.41, 11.85.

**HRMS** (EI-ESI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>24</sub>O<sub>4</sub> 424.1669; Found 424.1674.

### **7-benzyl-3-methyl-2-phenyl-8-(p-tolyl)-4H-chromen-4-one (6b)**

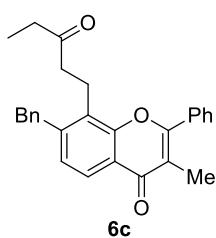


Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **6b** as a white solid. 50% yield (20.8 mg). m.p. 143–144 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.45–7.33 (m, 5H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.22 (td, *J* = 6.4, 3.0 Hz, 4H), 7.19–7.13 (m, 3H), 6.98 (d, *J* = 7.0 Hz, 2H), 3.95 (s, 2H), 2.40 (s, 3H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 179.26, 160.65, 154.04, 145.31, 140.42, 137.47, 133.48, 131.71, 131.40, 130.07, 129.12, 129.04, 128.99, 128.53, 128.29, 126.79, 126.28,

124.66, 120.89, 117.07, 39.41, 21.45, 12.01. **HRMS** (EI-ESA)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub> 416.1771; Found 416.1758.

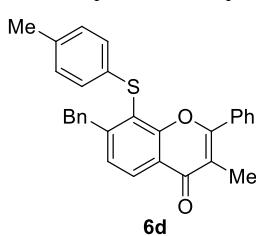
**7-benzyl-3-methyl-8-(3-oxopentyl)-2-phenyl-4H-chromen-4-one (6c)**



Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 40:1) afforded **6c** as a white solid. 49% yield (20.1 mg). m.p. 117-118 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.10 (d,  $J$  = 8.1 Hz, 1H), 7.67-7.57 (m, 2H), 7.54-7.47 (m, 3H), 7.28-7.24 (m, 3H), 7.19 (t,  $J$  = 7.4 Hz, 1H), 7.11 (d,  $J$  = 7.1 Hz, 2H), 4.17 (s, 2H), 3.17-3.05 (m, 2H), 2.39-2.27 (m, 2H), 2.23-2.13 (m, 5H), 0.92 (t,  $J$  = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 210.36, 179.21, 160.65, 154.92, 144.84, 140.02, 133.67, 130.37, 128.97, 128.85, 128.81, 128.78, 128.68, 127.61, 126.55, 123.74, 121.31, 117.43, 41.35, 39.83, 35.85, 20.82, 11.88, 7.89. **HRMS** (EI-ESA)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>26</sub>O<sub>3</sub> 410.1876; Found 410.1868.

**7-benzyl-3-methyl-2-phenyl-8-(p-tolylthio)-4H-chromen-4-one (6d)**



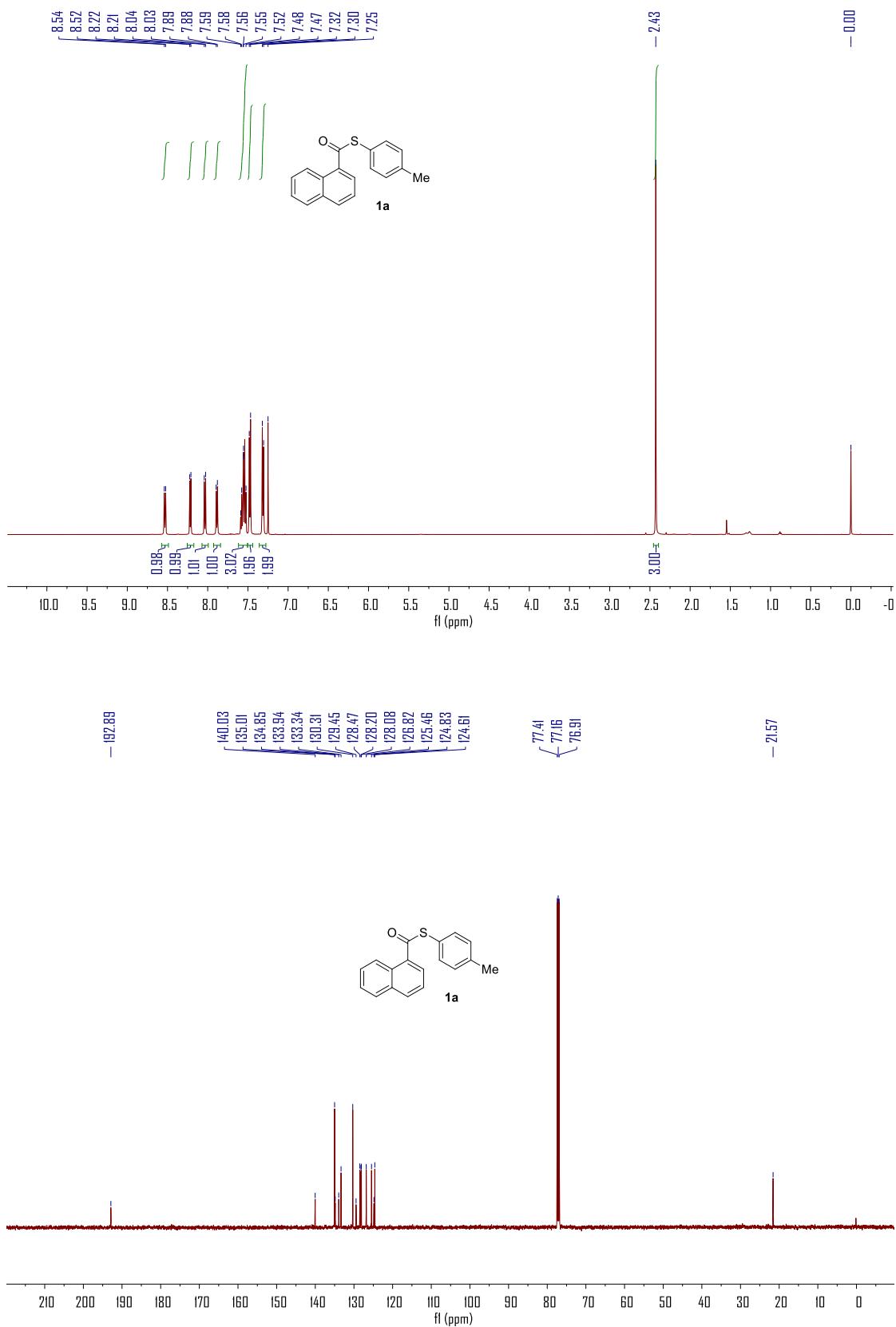
Purification by flash column chromatography on silica gel (Hexanes/EtOAc = 50:1) afforded **6d** as a white solid. 31% yield (13.9 mg). m.p. 122-124 °C.

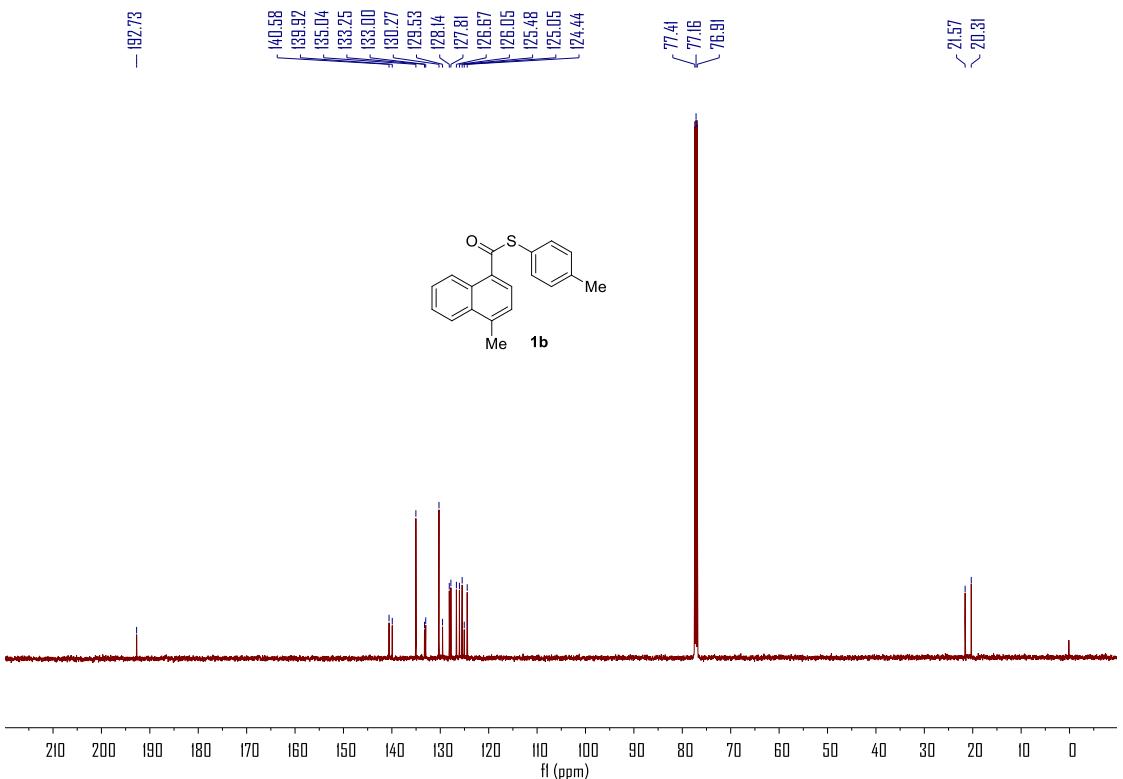
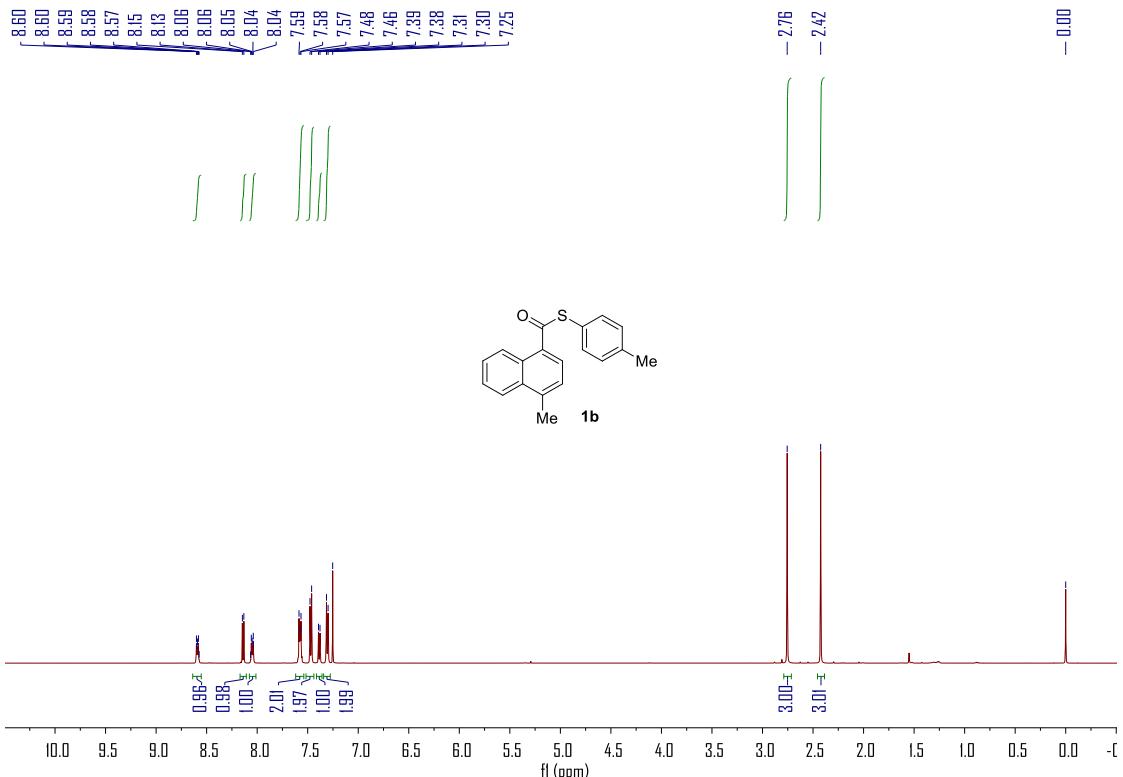
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.22 (d,  $J$  = 8.3 Hz, 1H), 7.43 (tt,  $J$  = 6.9, 1.3 Hz, 1H), 7.37-7.32 (m, 3H), 7.30-7.24 (m, 2H), 7.22-7.17 (m, 3H), 7.13-7.11 (m, 2H), 6.99 (d,  $J$  = 8.1 Hz, 2H), 6.92 (d,  $J$  = 8.3 Hz, 2H), 4.45 (s, 2H), 2.29 (s, 3H), 2.13 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 178.99, 161.19, 156.44, 151.52, 139.86, 135.89, 133.29, 133.07, 130.20, 129.85, 129.28, 129.15, 128.77, 128.26, 127.83, 127.04, 126.60, 126.55, 122.08, 121.92, 117.51, 40.82, 21.07, 11.79. **HRMS** (EI-ESA)  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub>S 448.1492; Found 448.1483.

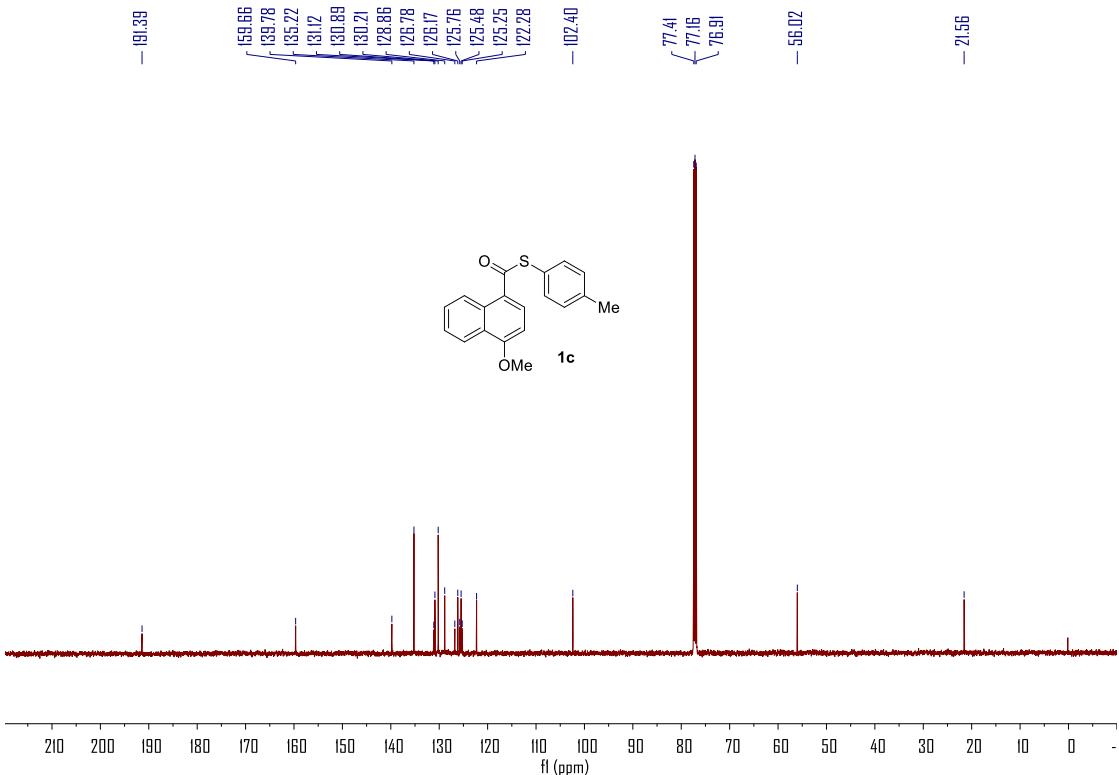
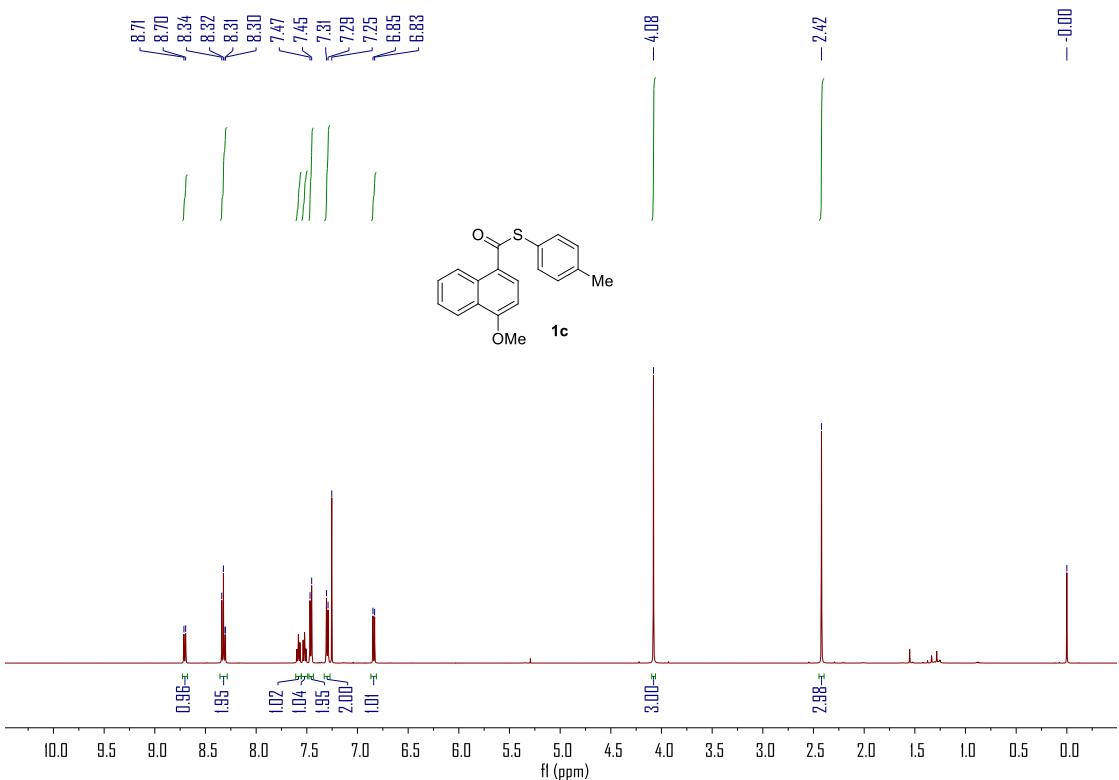
**REFERENCES**

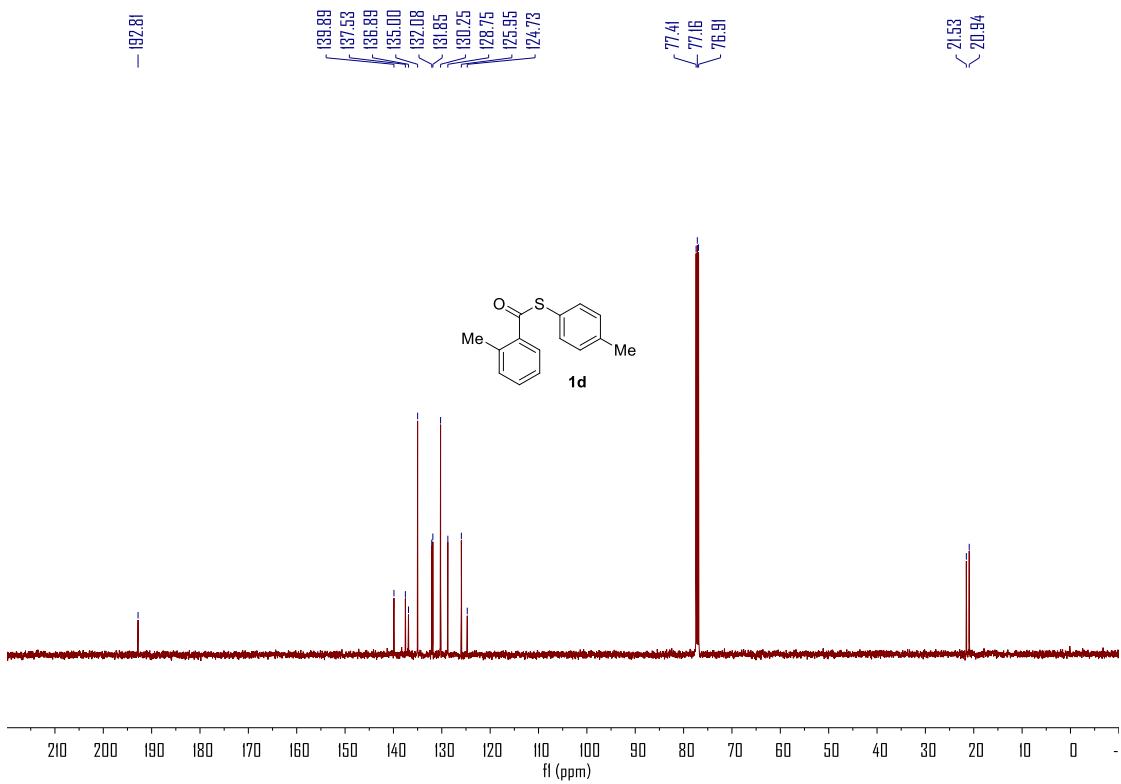
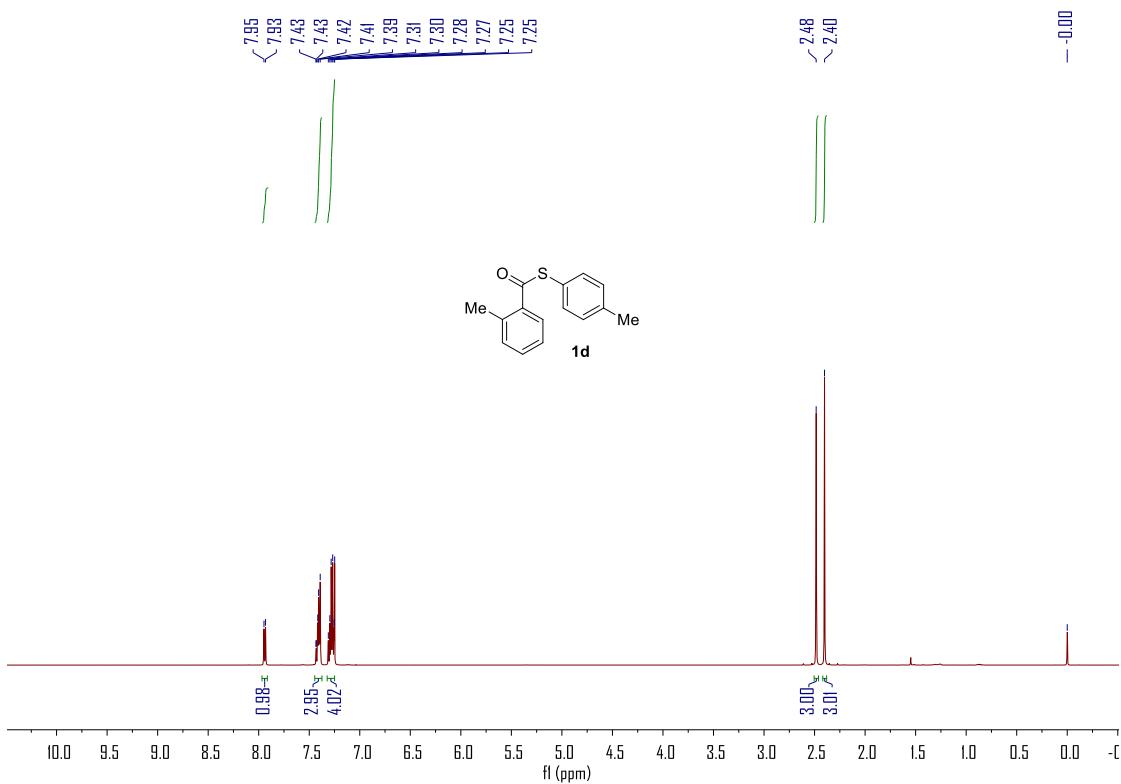
1. Zhu, C., Zhang, Y., Kan, J., Zhao, H. & Su, W. Ambient-temperature ortho C–H arylation of benzoic acids with aryl iodides with ligand-supported palladium catalyst. *Org. Lett.* **17**, 3418–3421 (2015).
2. Weis, E., Johansson, M. J. & Martín-Matute, B. Ir<sup>III</sup>-catalyzed selective *ortho*-monoiodination of benzoic acids with unbiased C–H bonds. *Chem. Eur. J.* **26**, 10185–10190 (2020).
3. Ye, C., Zhu, H. & Chen, Z. Synthesis of biaryl tertiary amines through Pd/norbornene joint catalysis in a remote C–H amination/Suzuki coupling reaction. *J. Org. Chem.* **79**, 8900–8905 (2014).

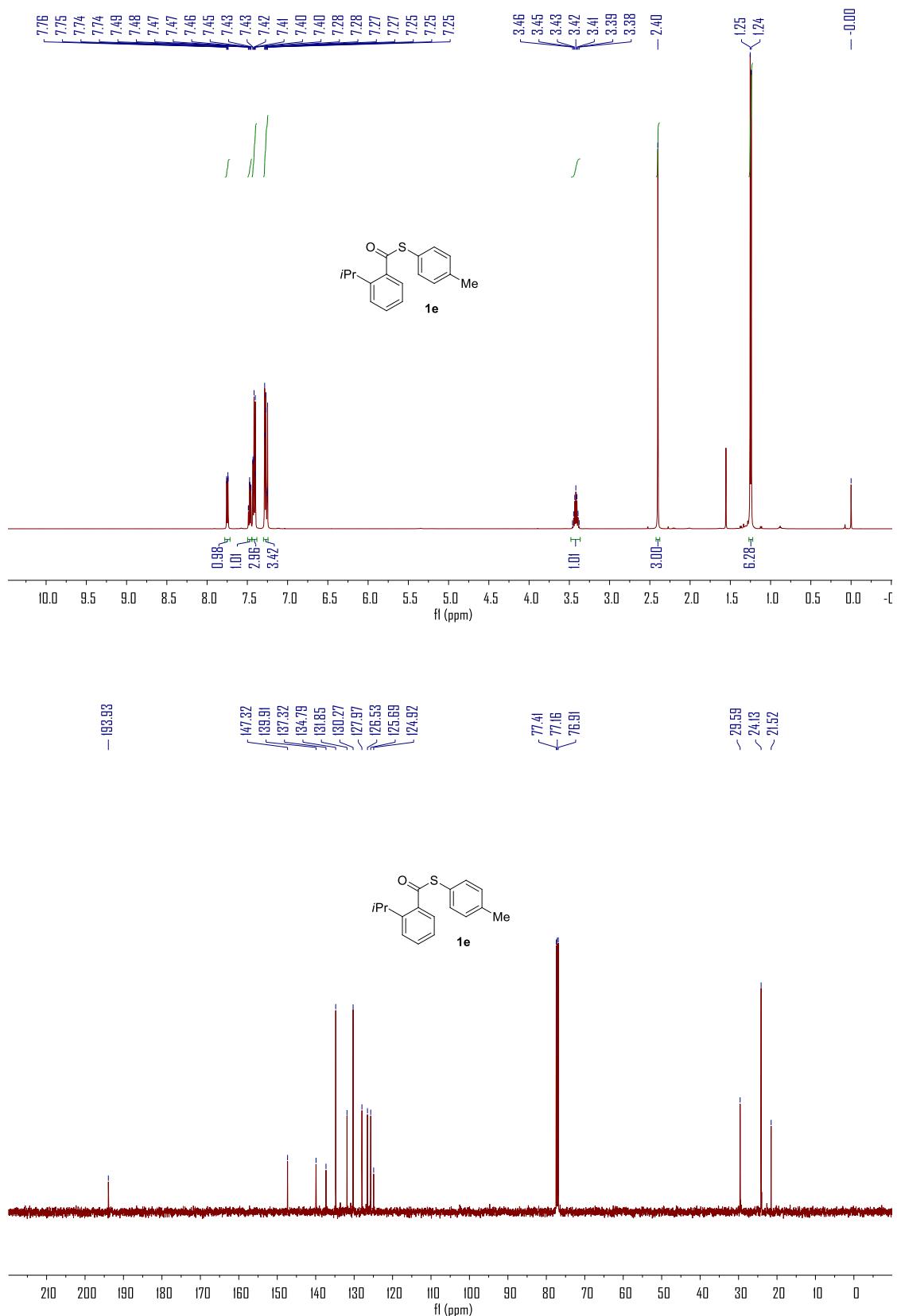
## 8. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

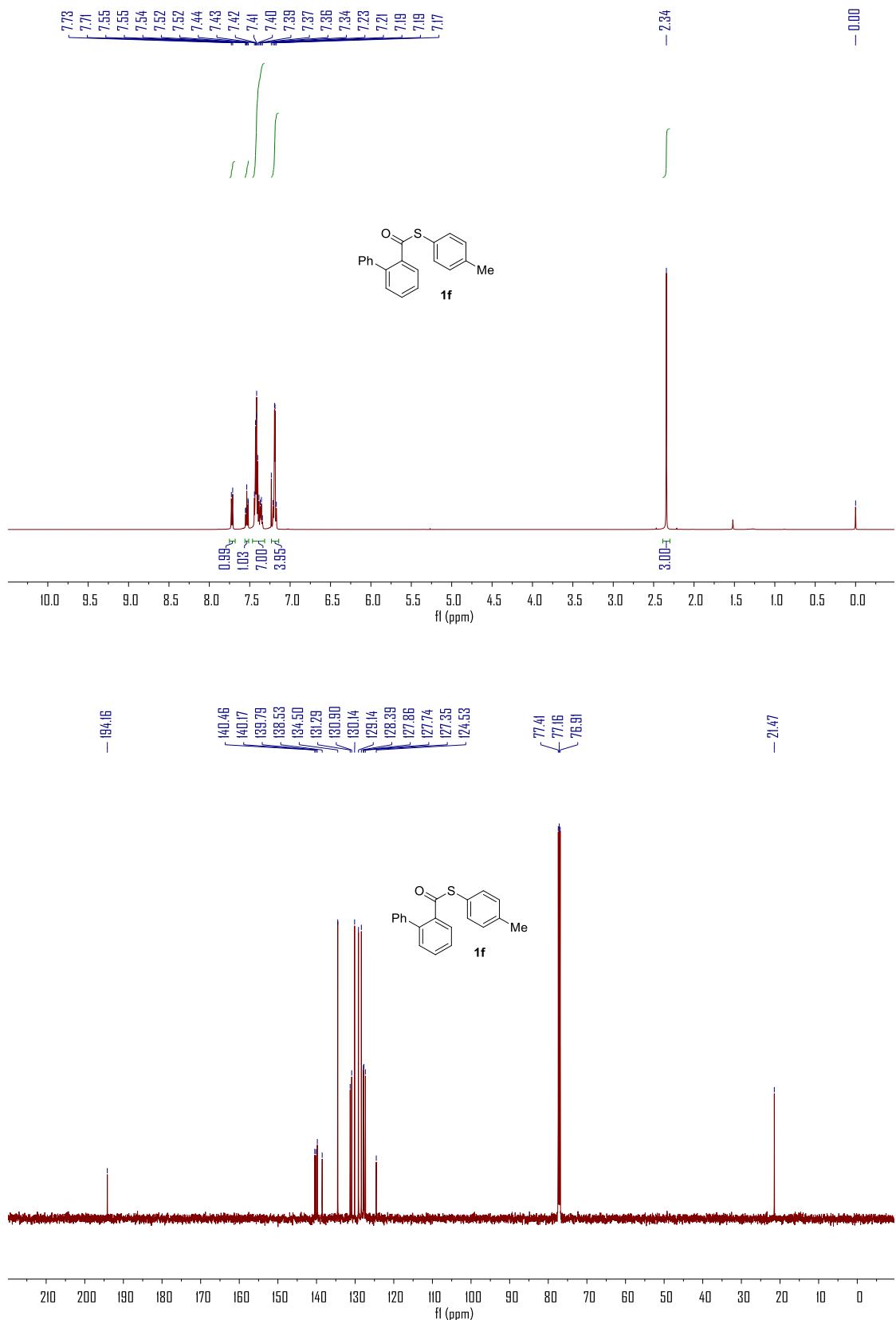


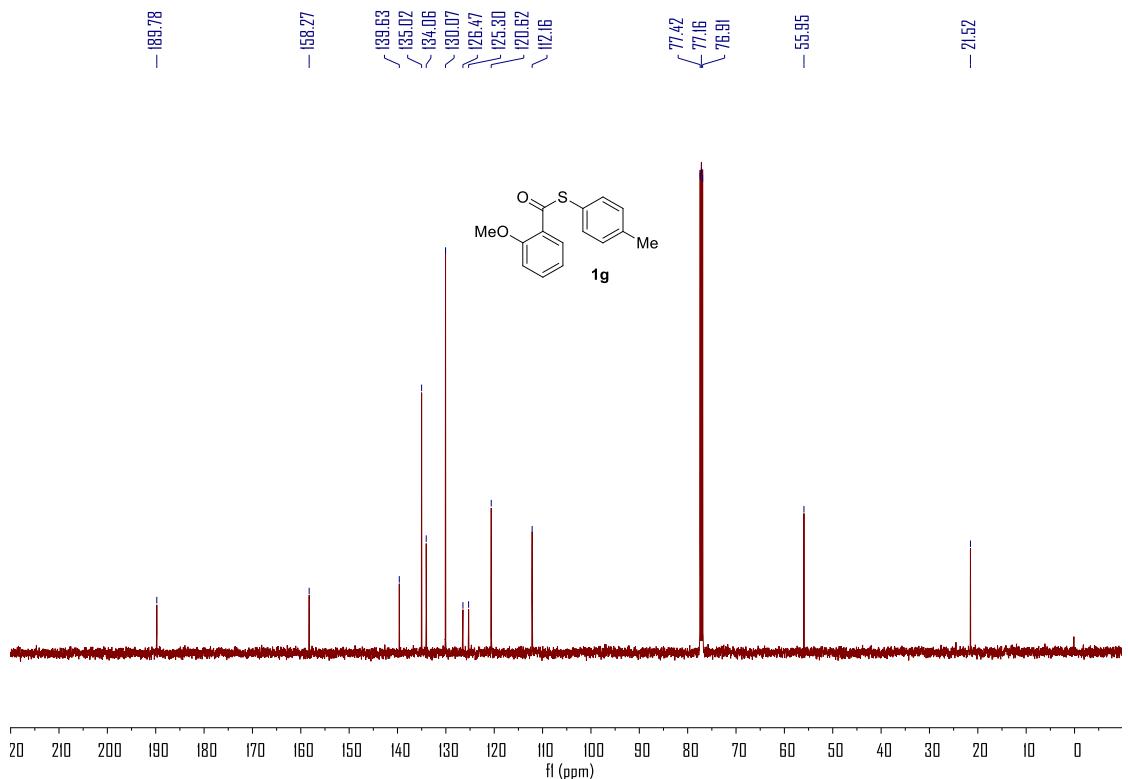
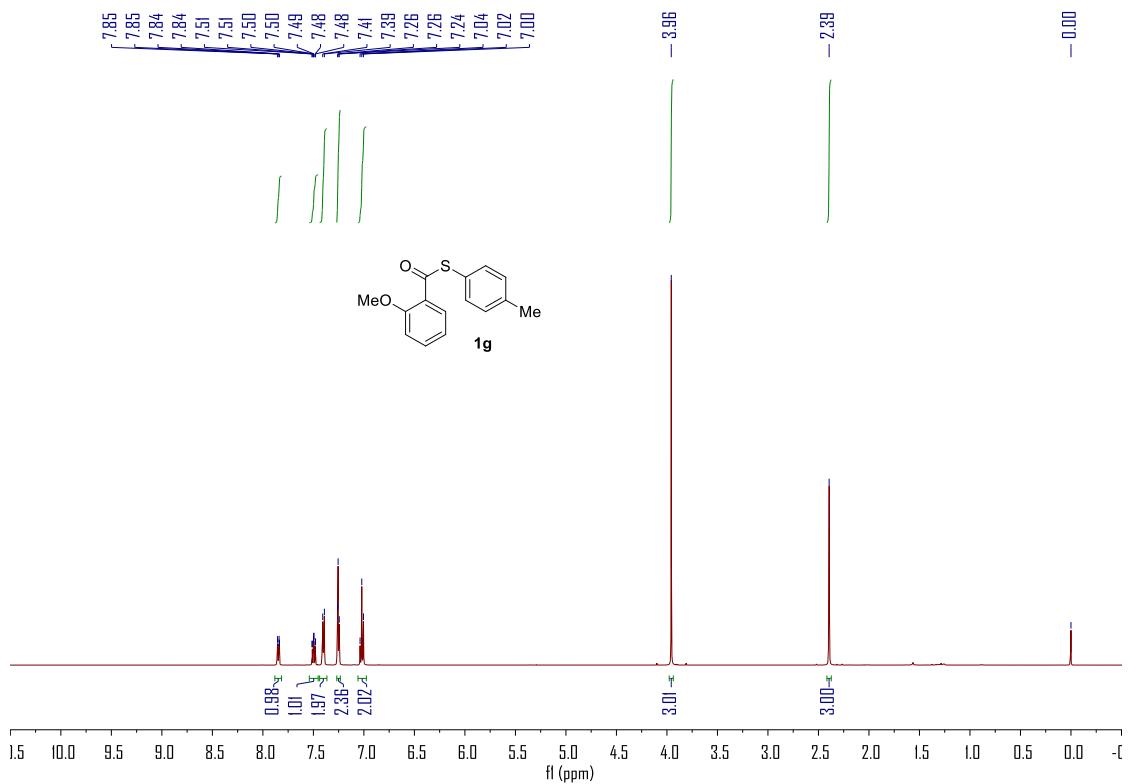


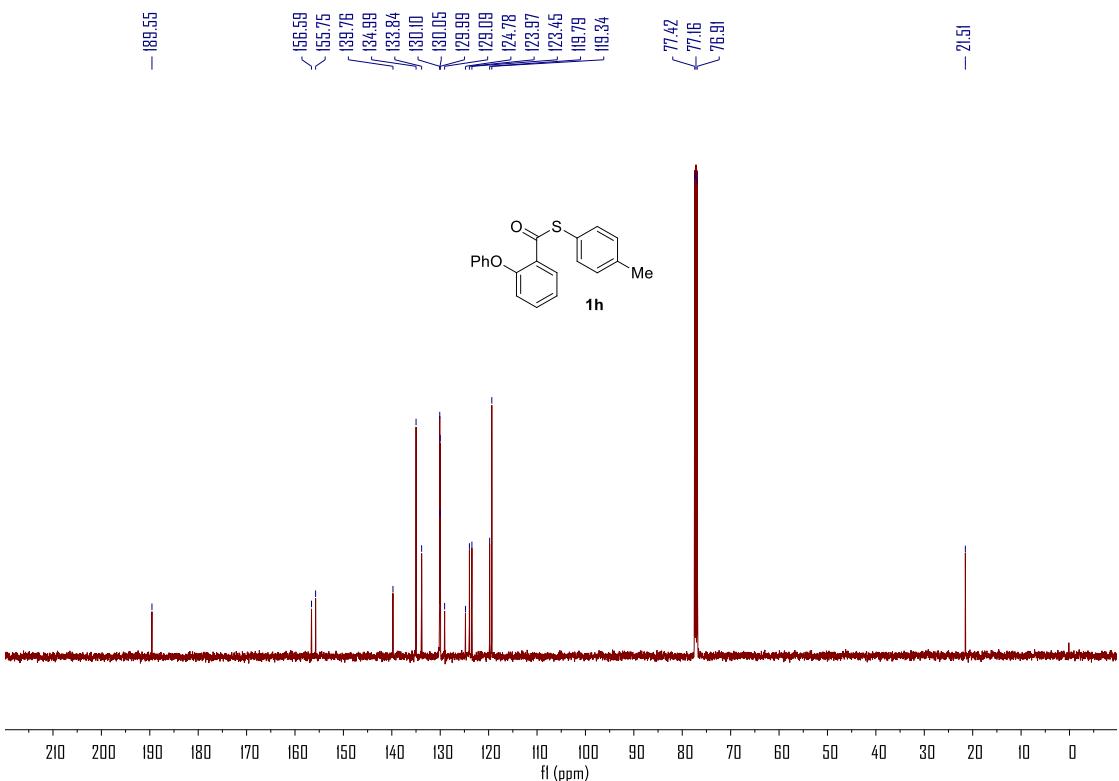
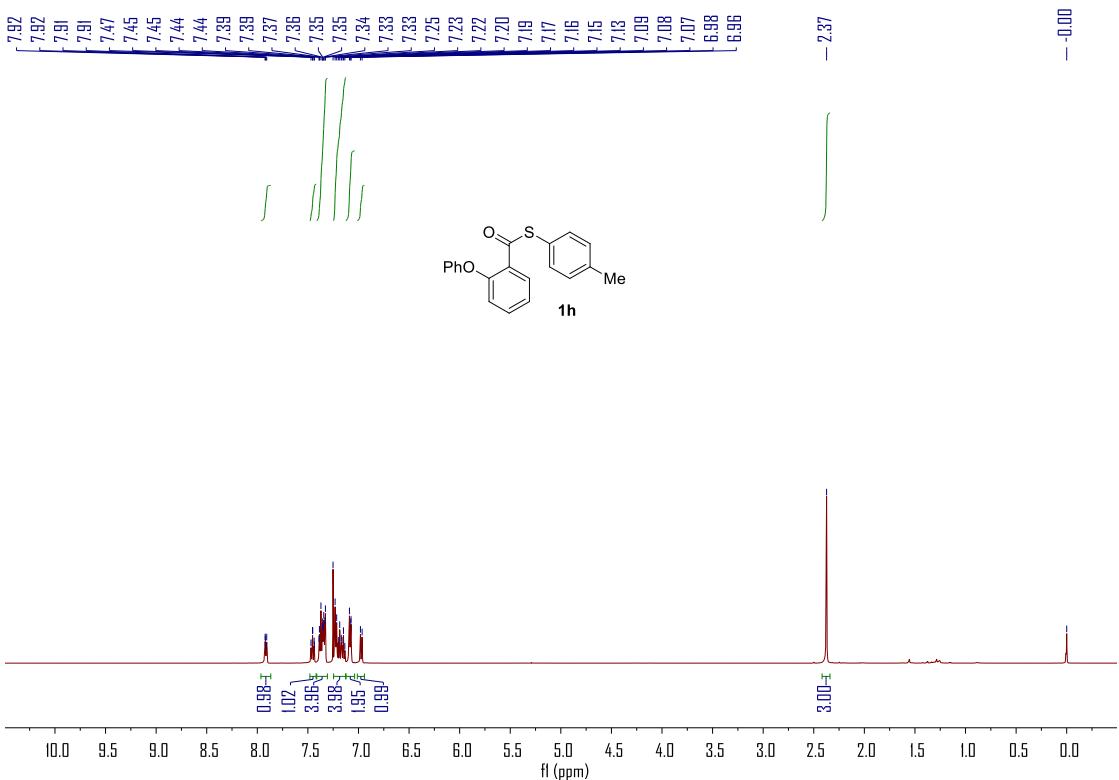


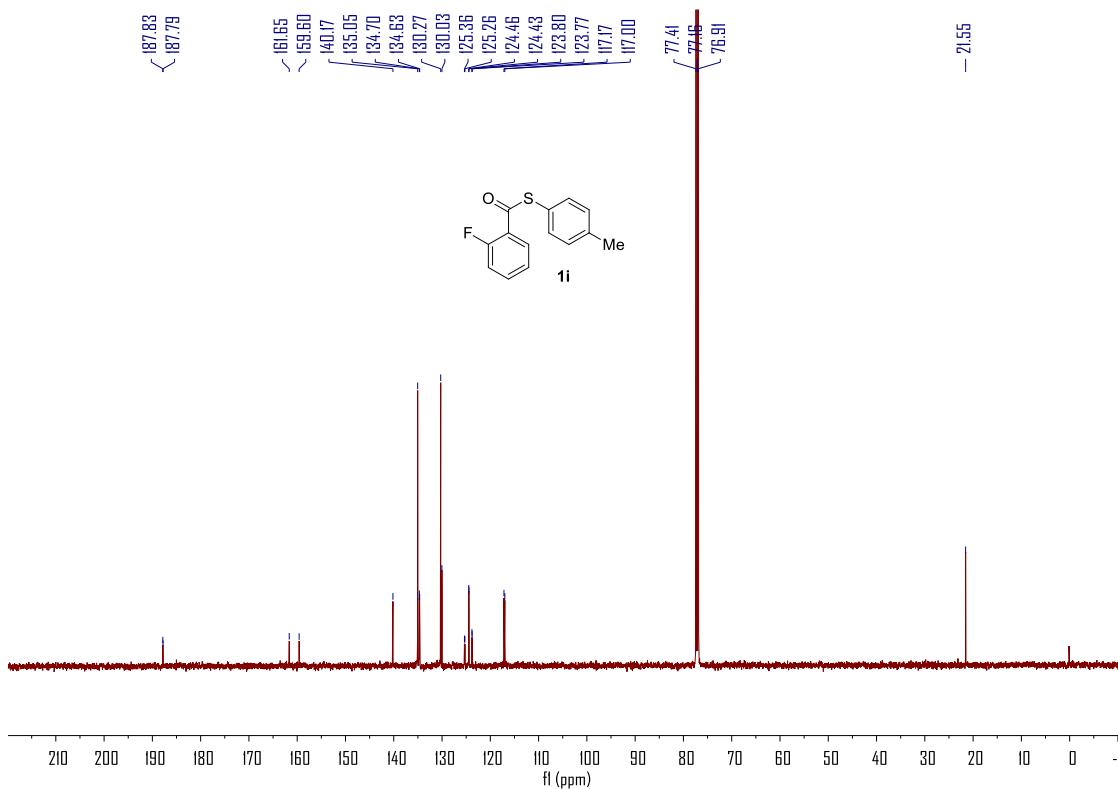
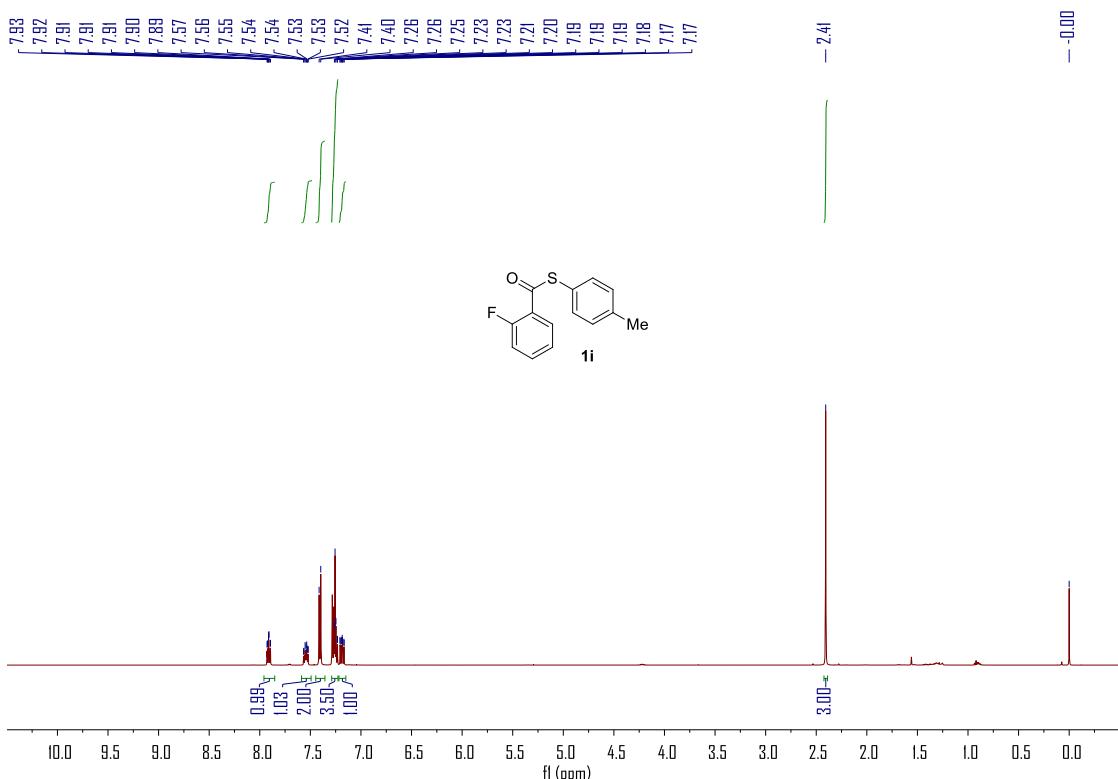




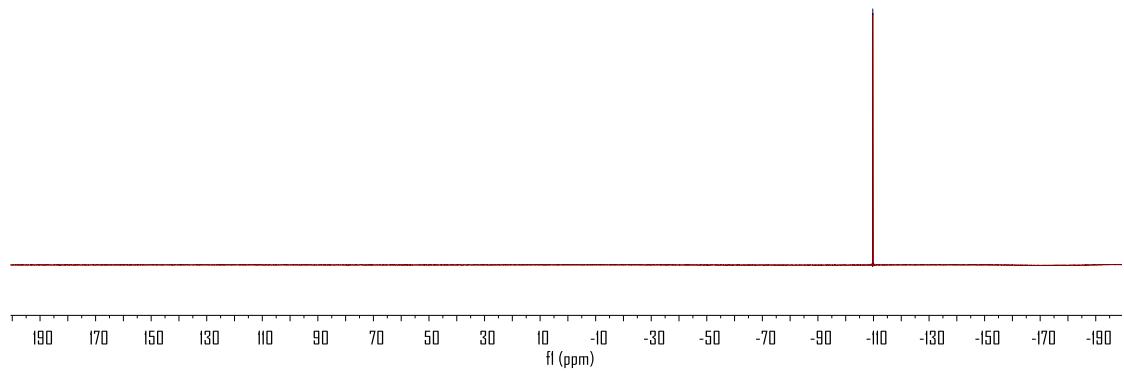
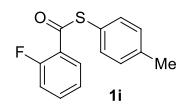


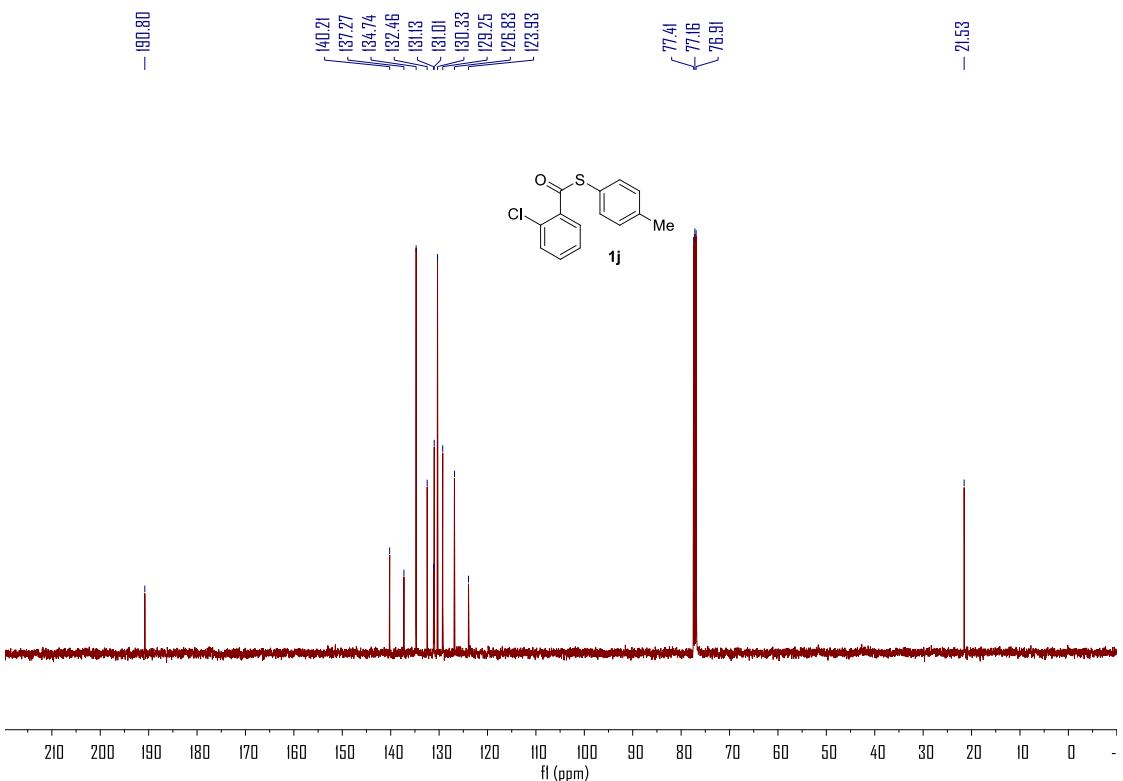
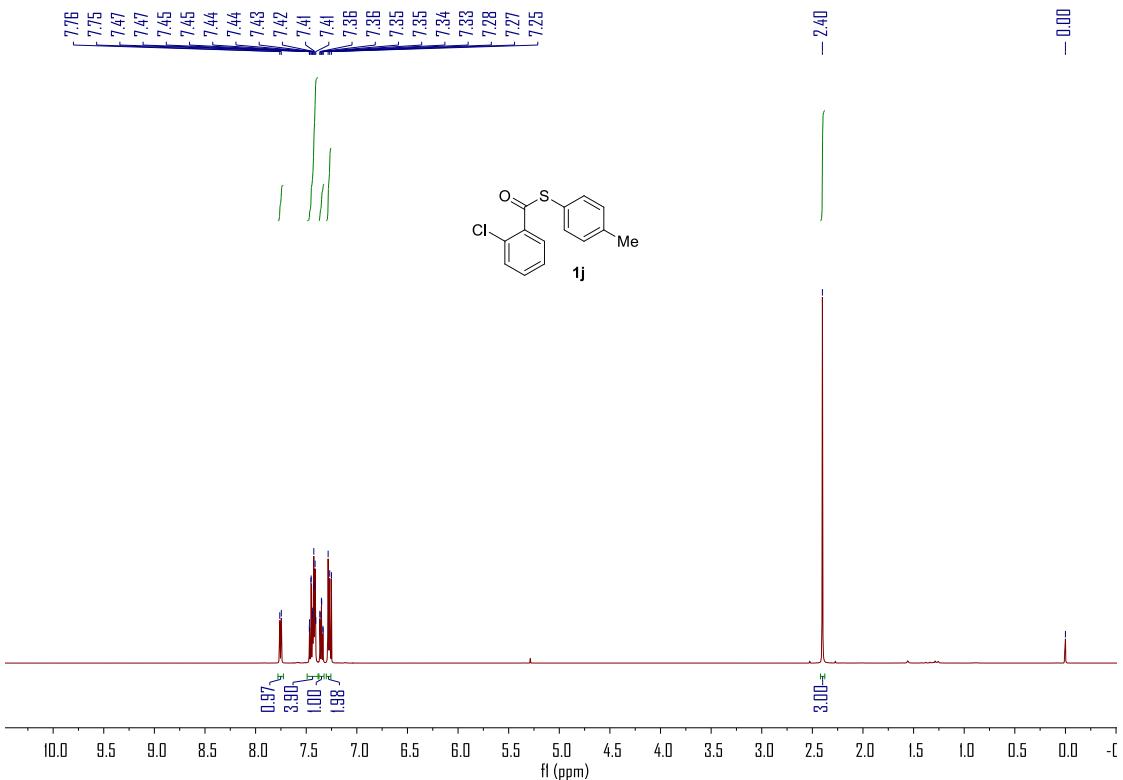


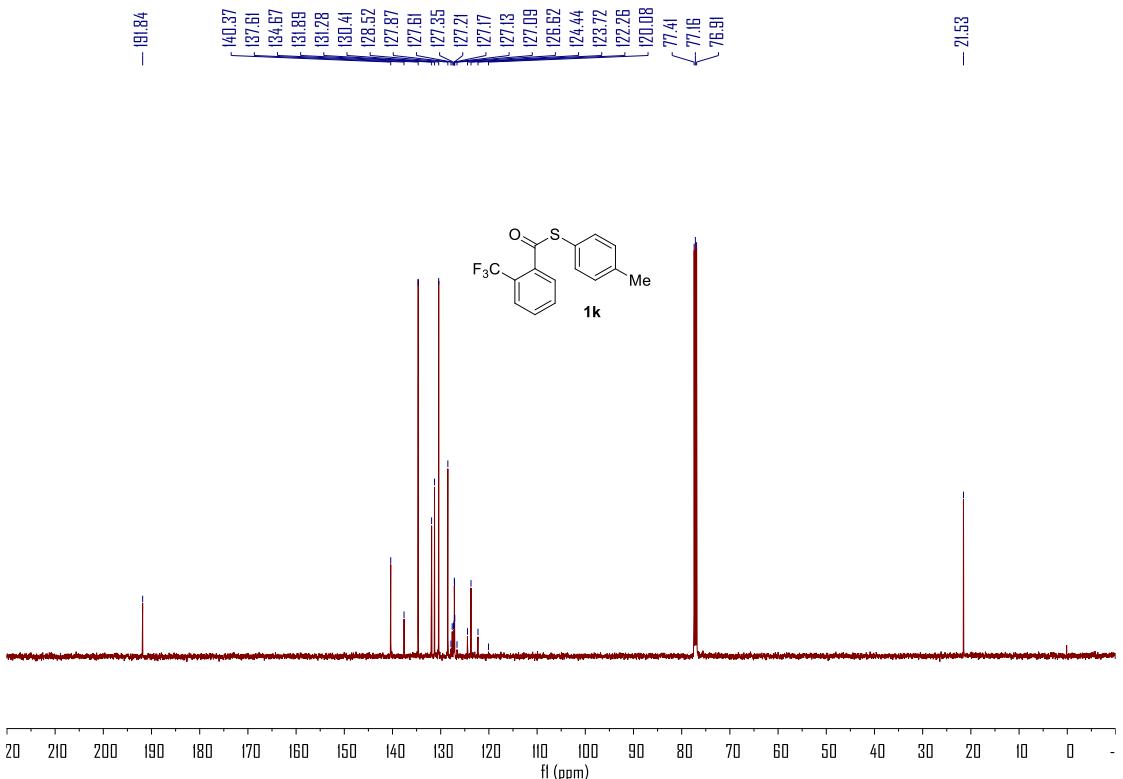
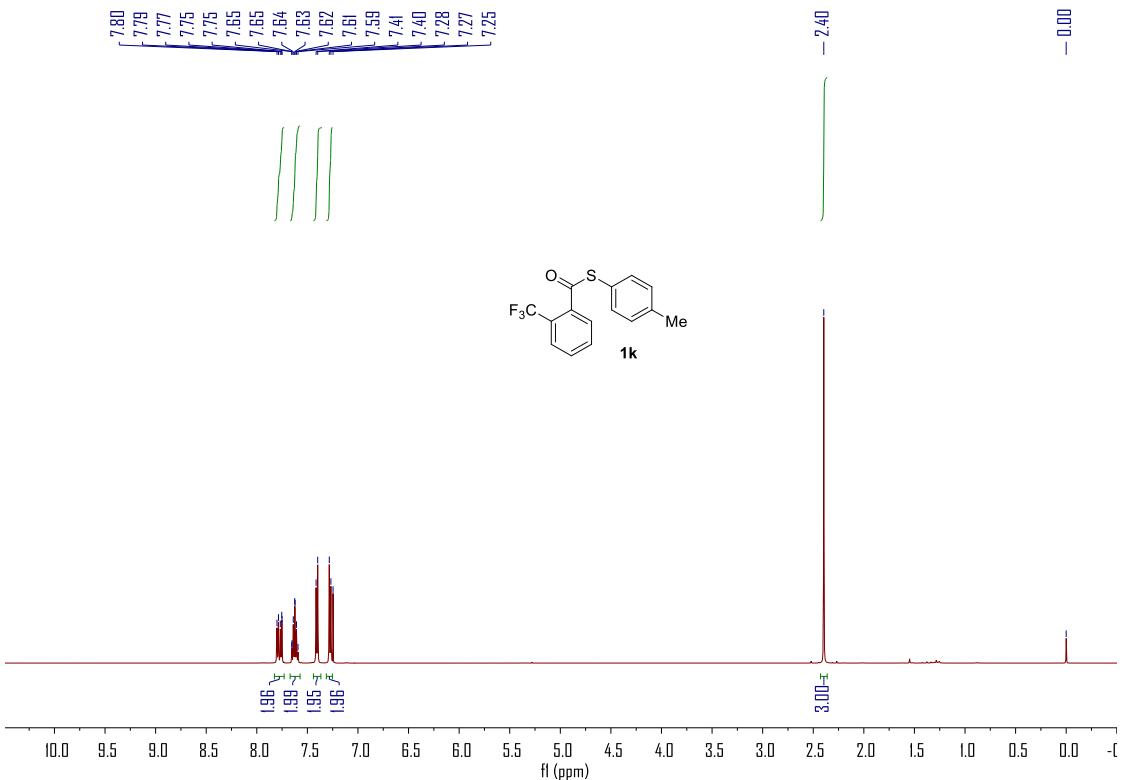


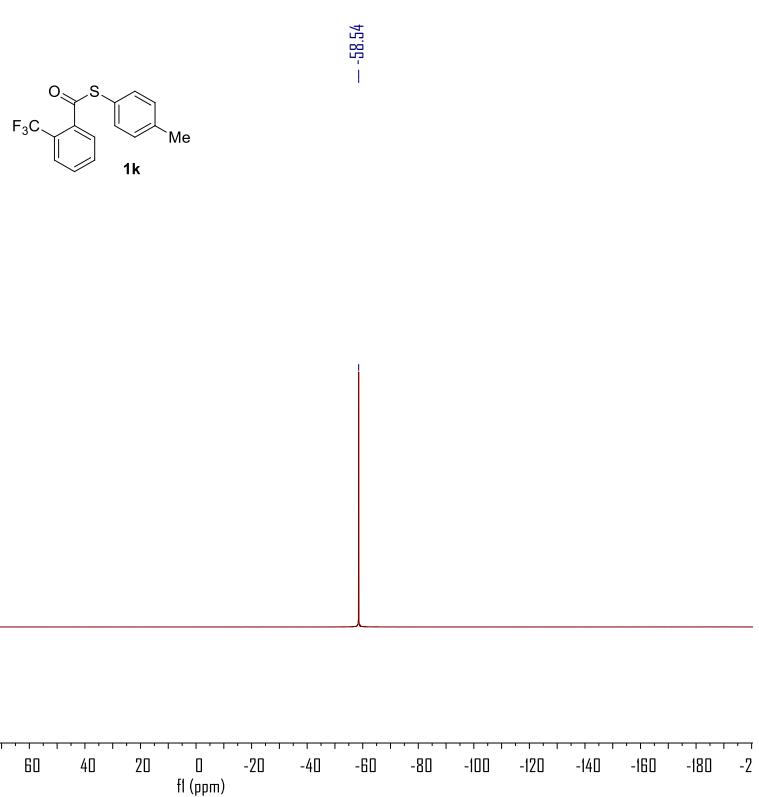


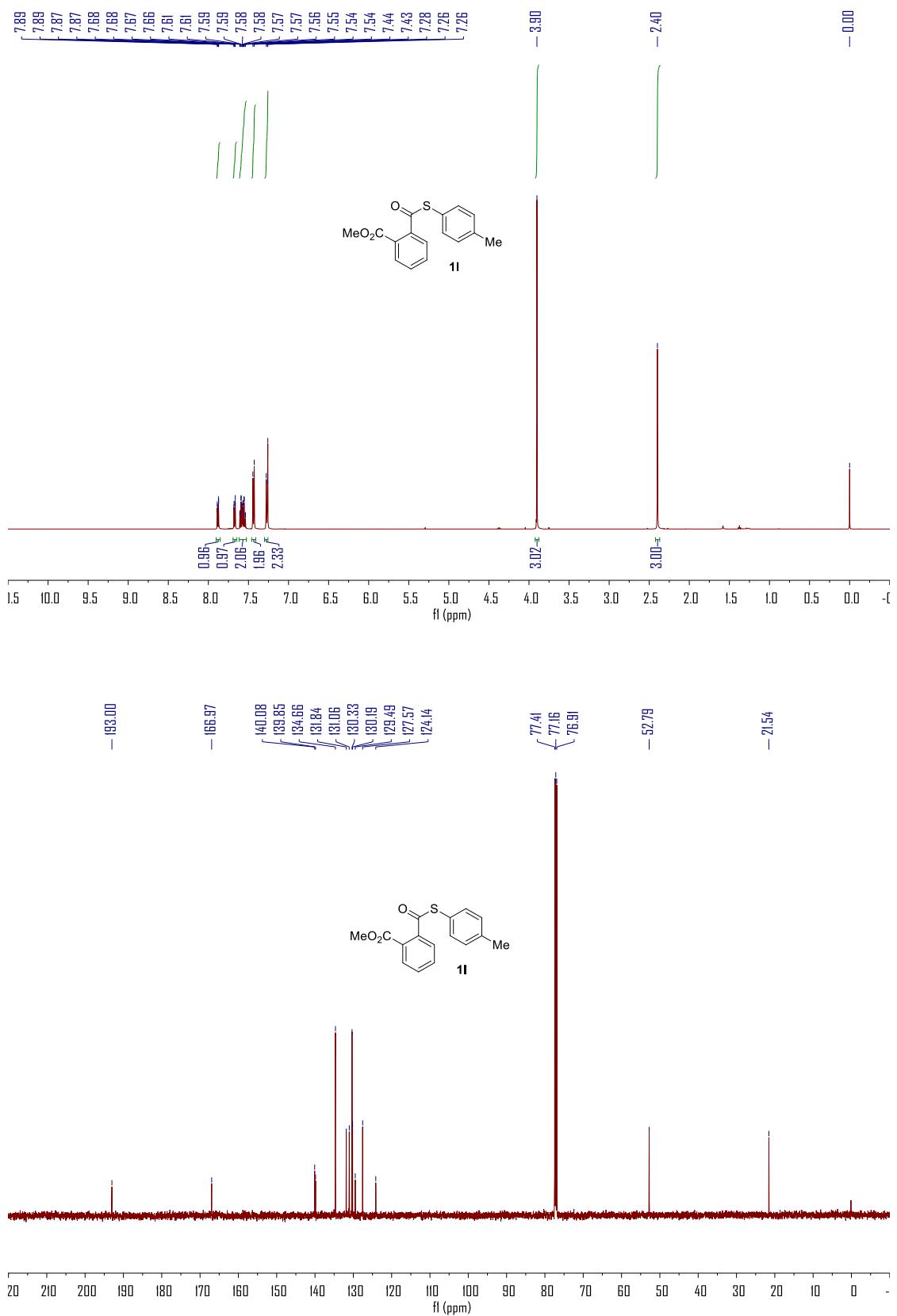
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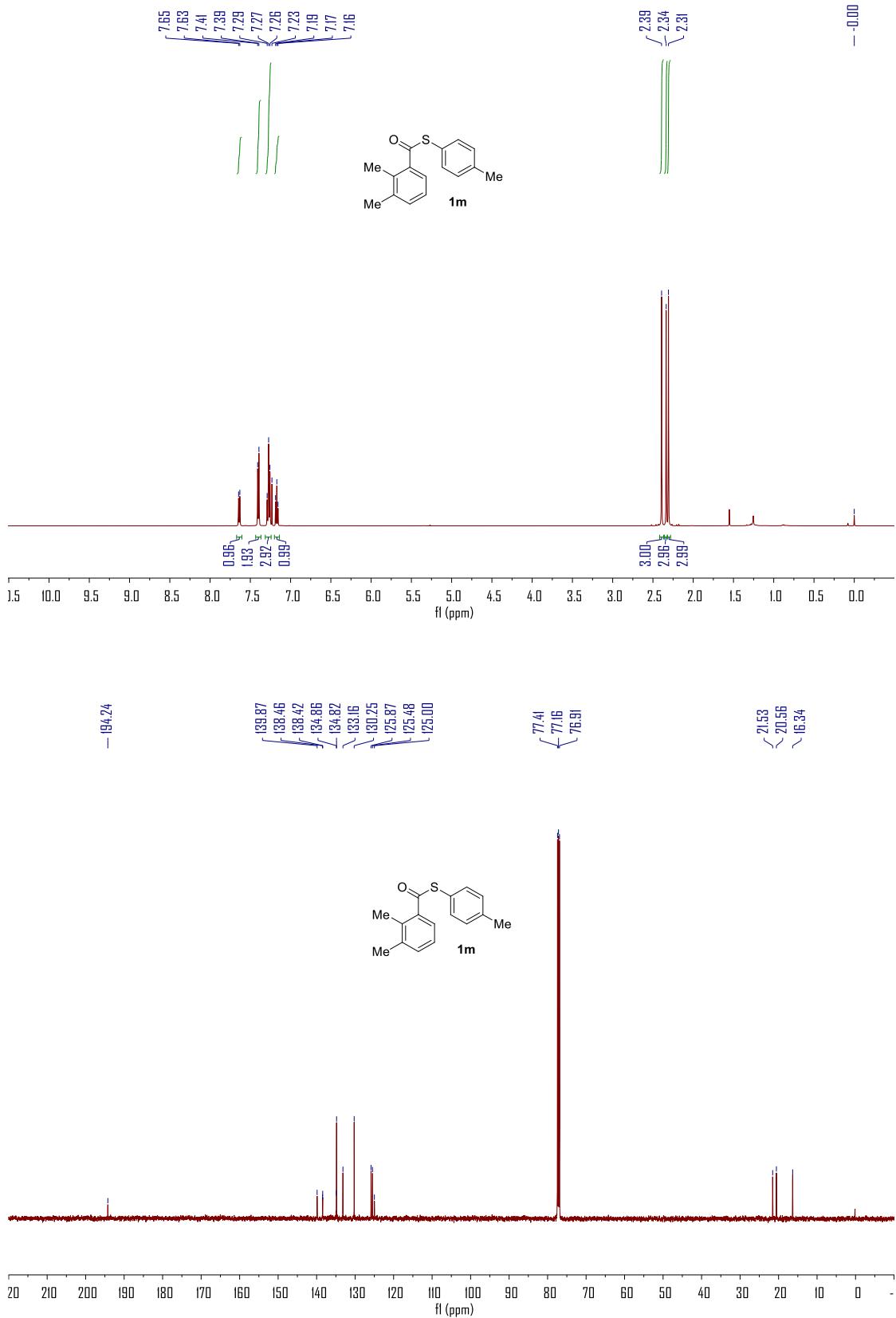


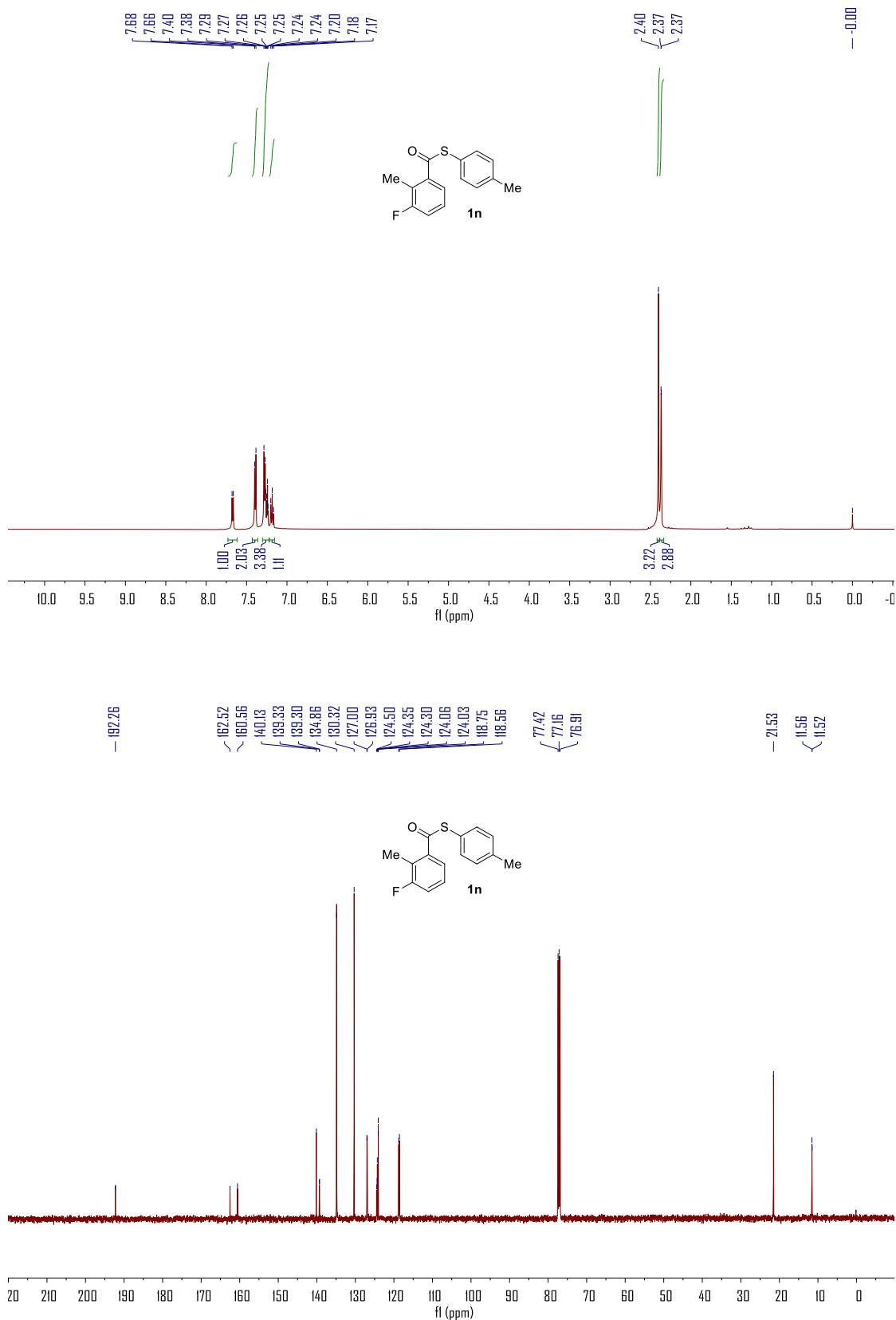


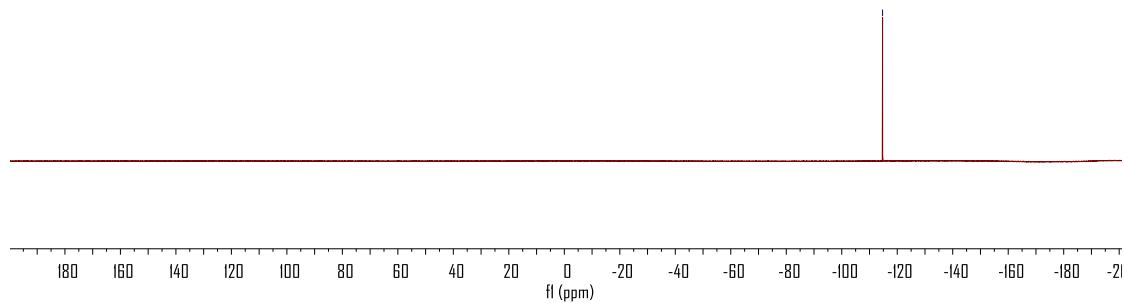
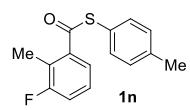


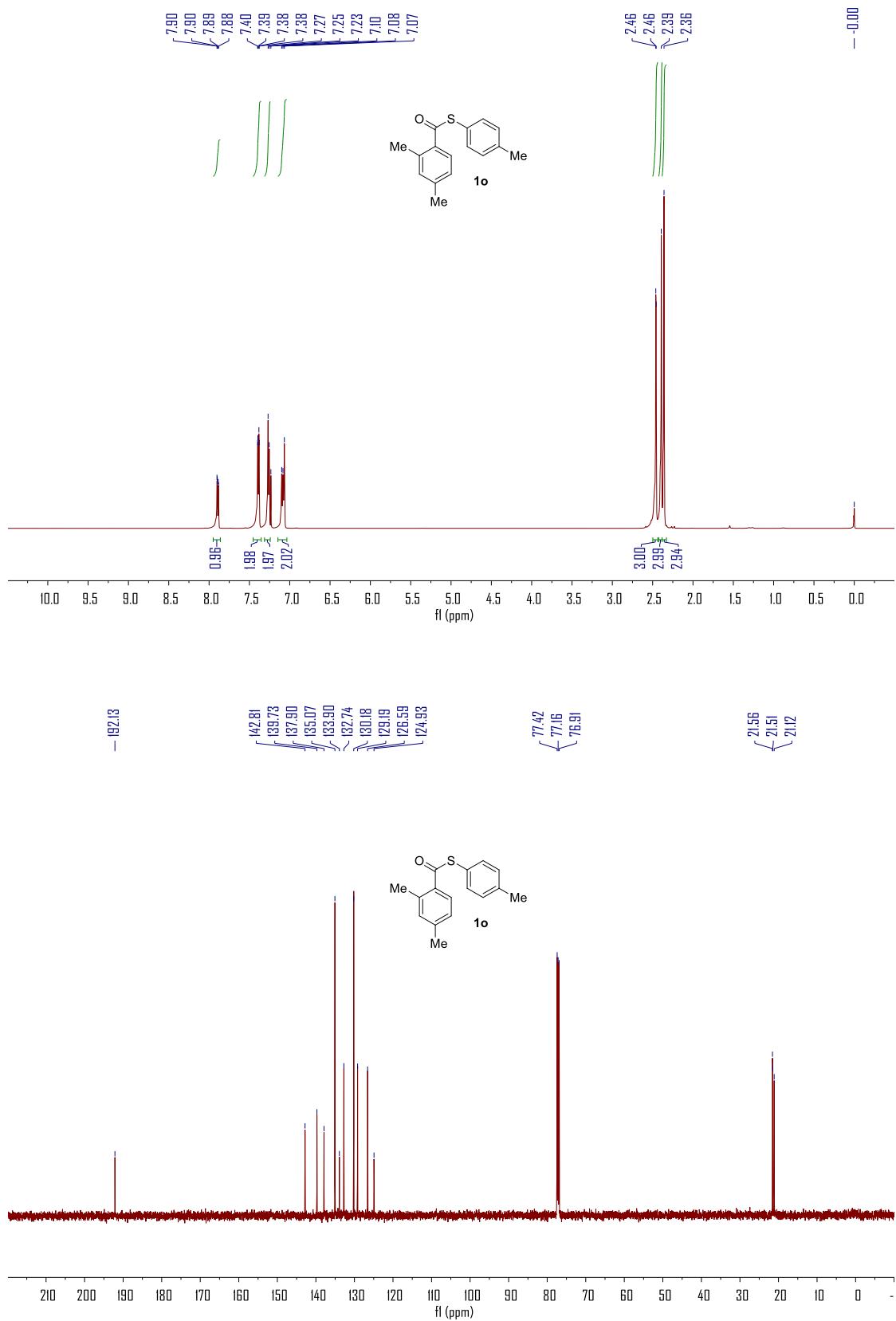


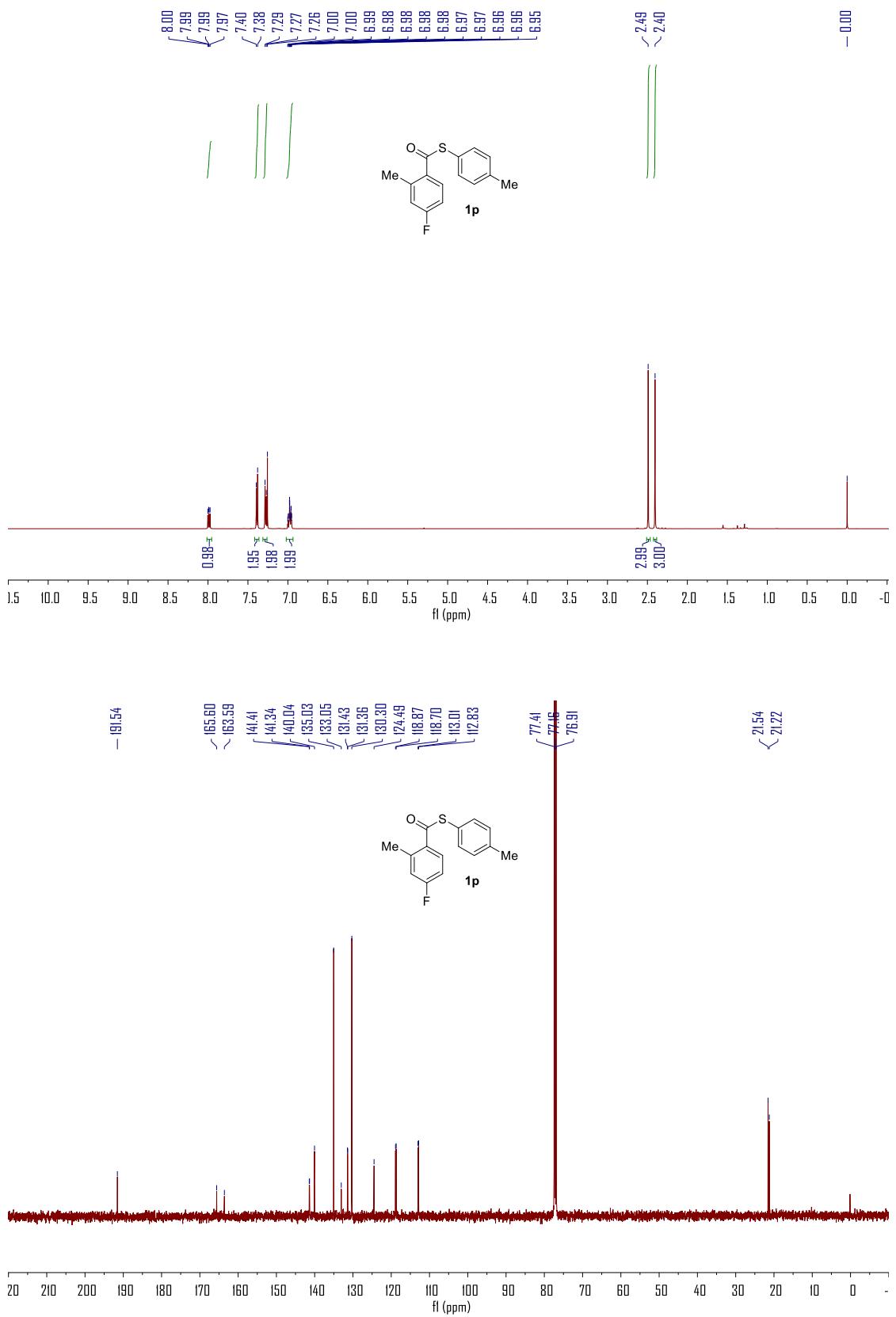




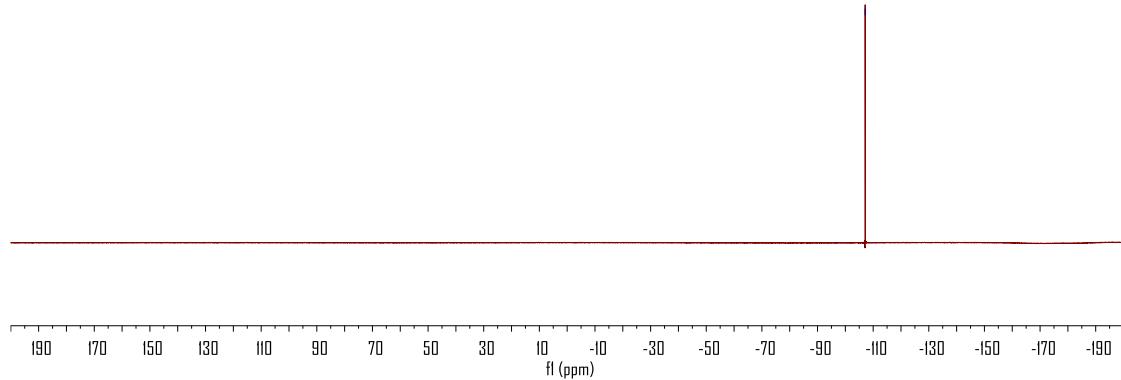
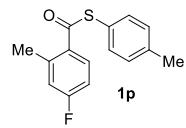


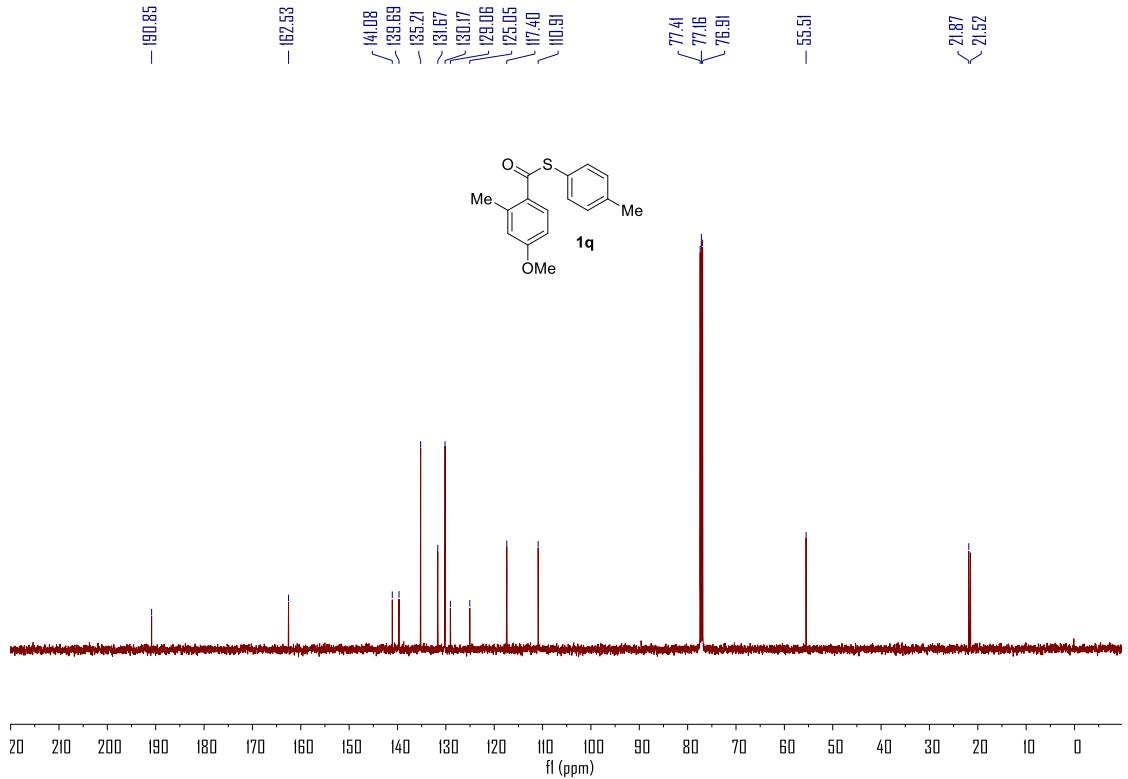
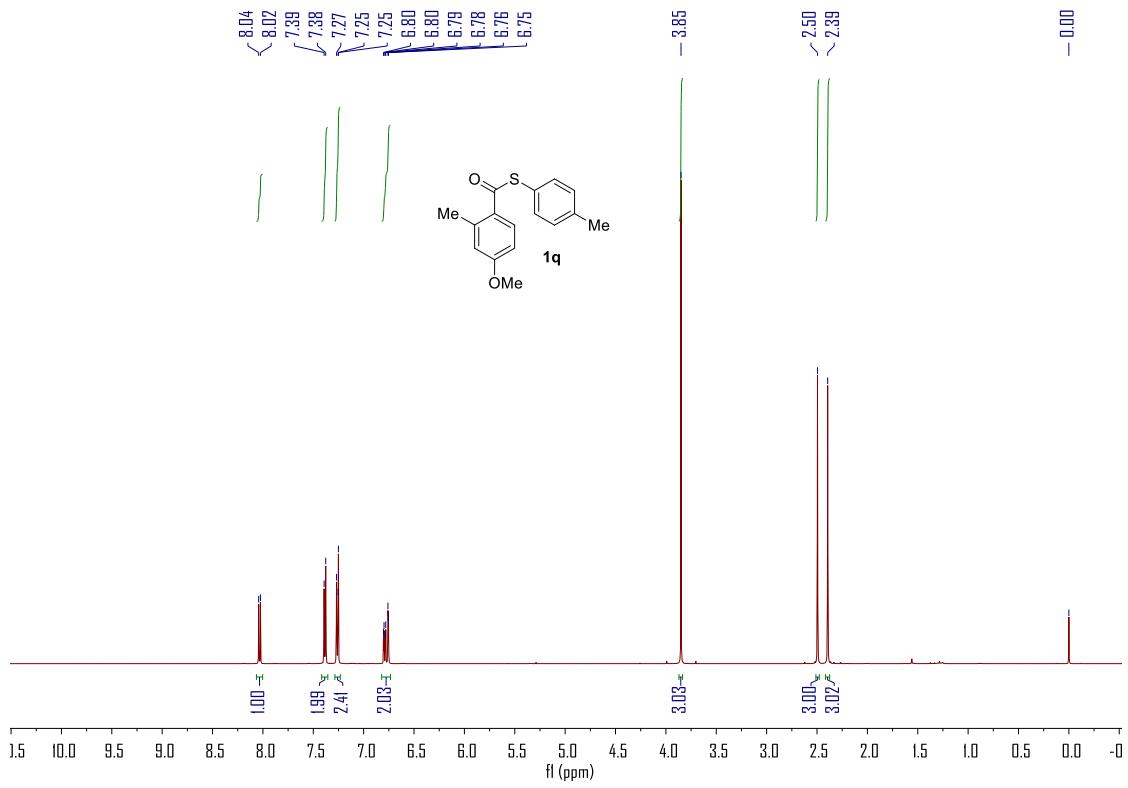


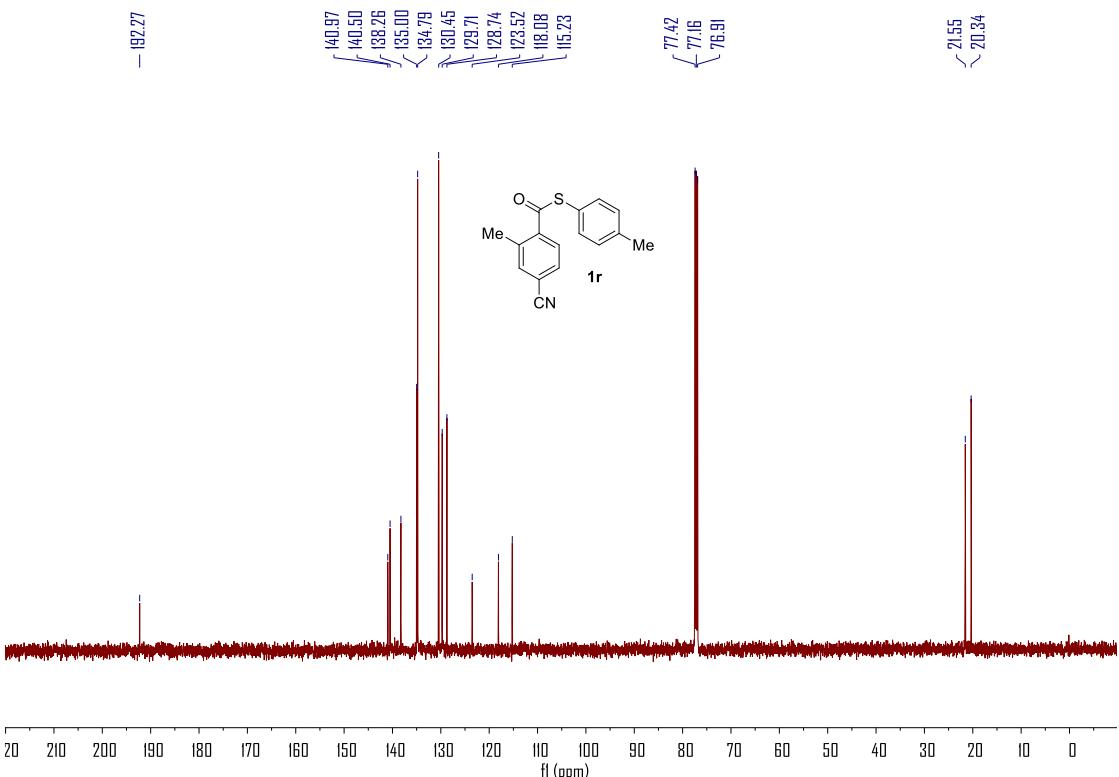
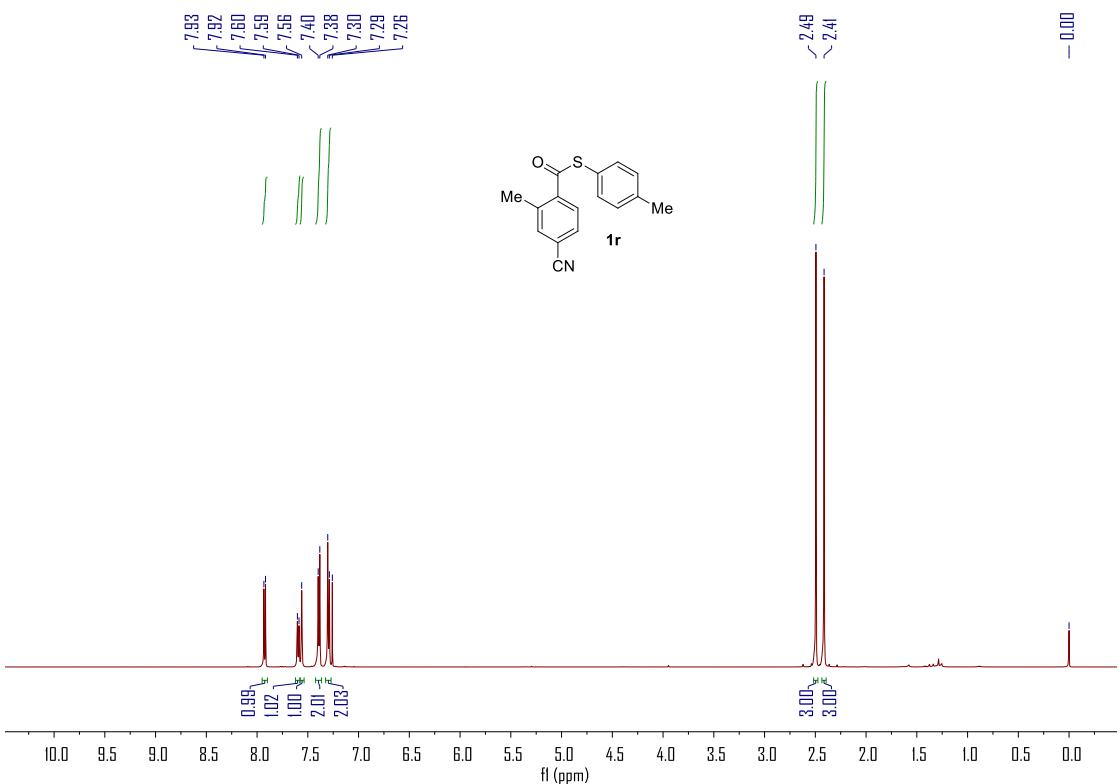


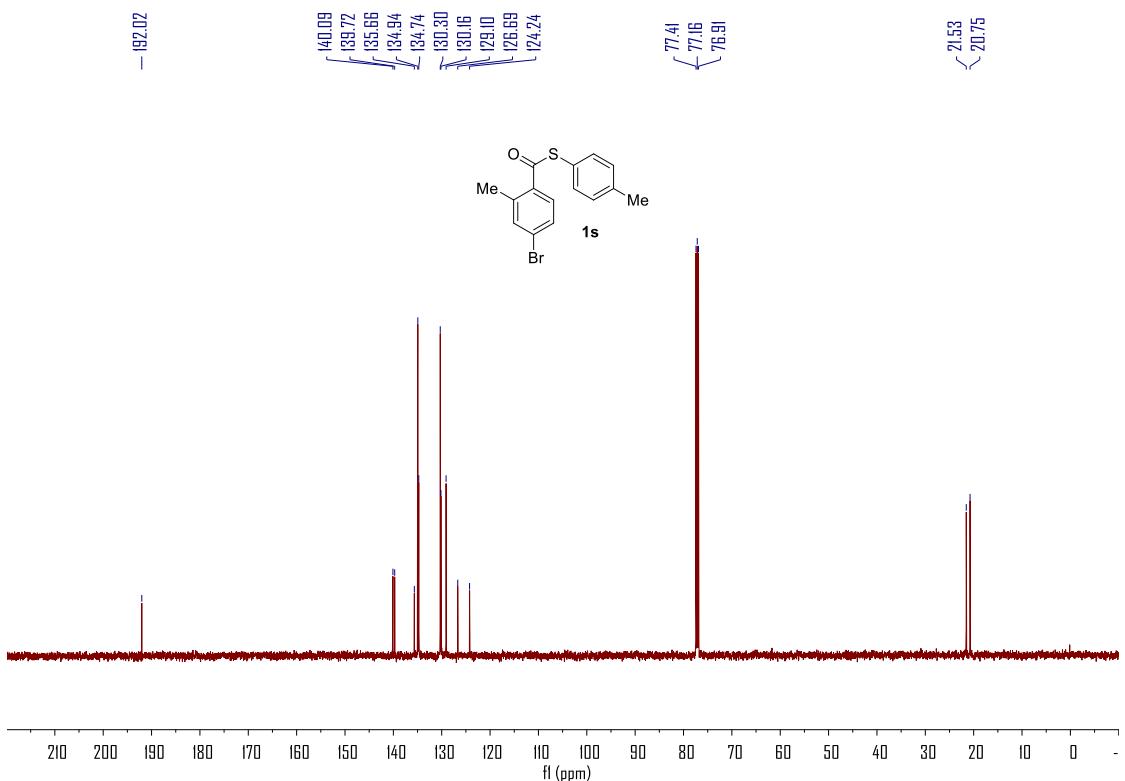
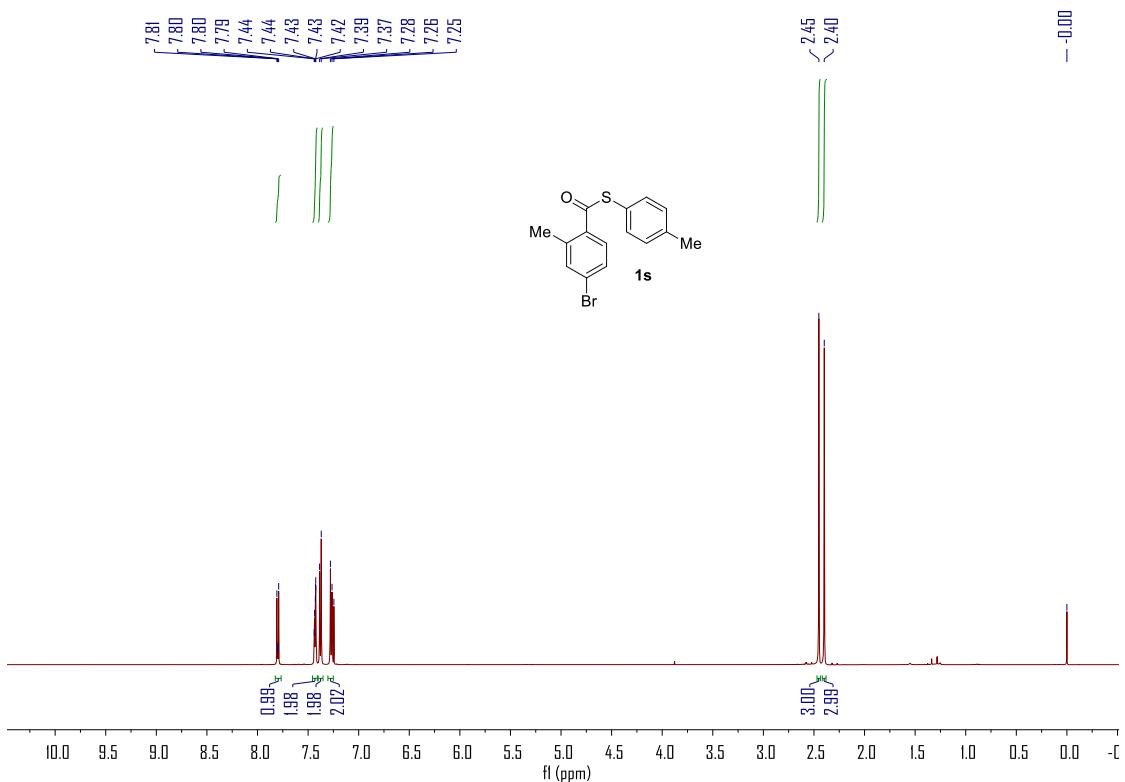


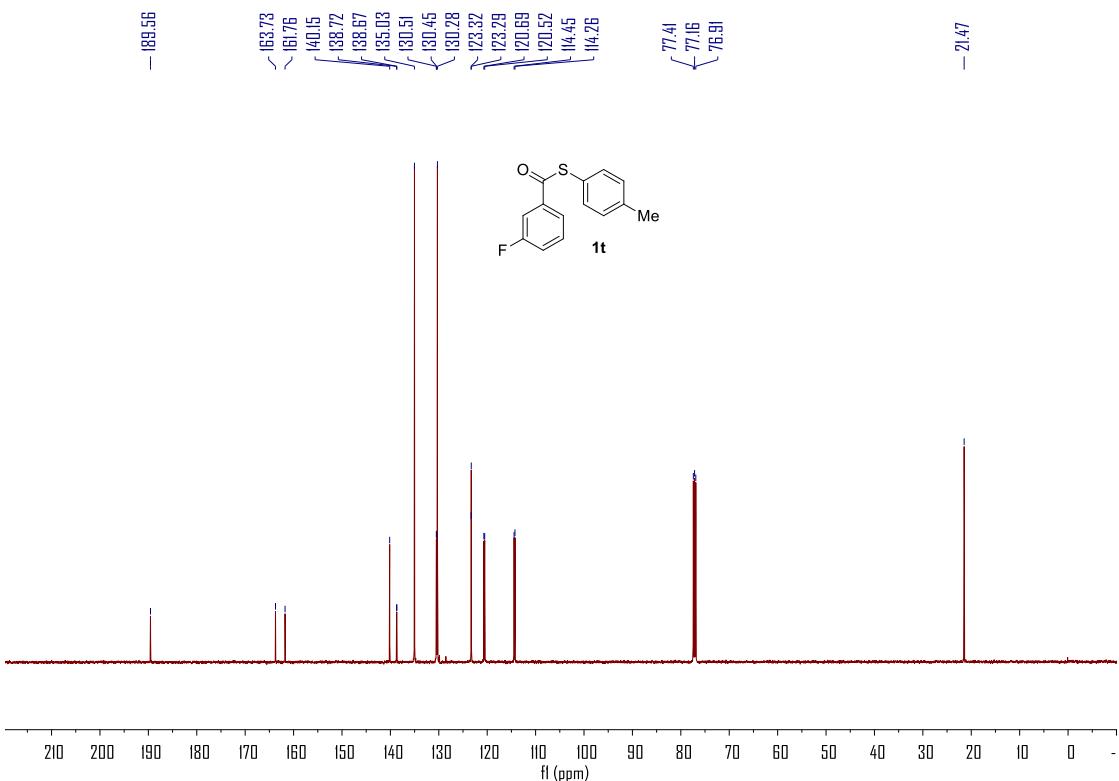
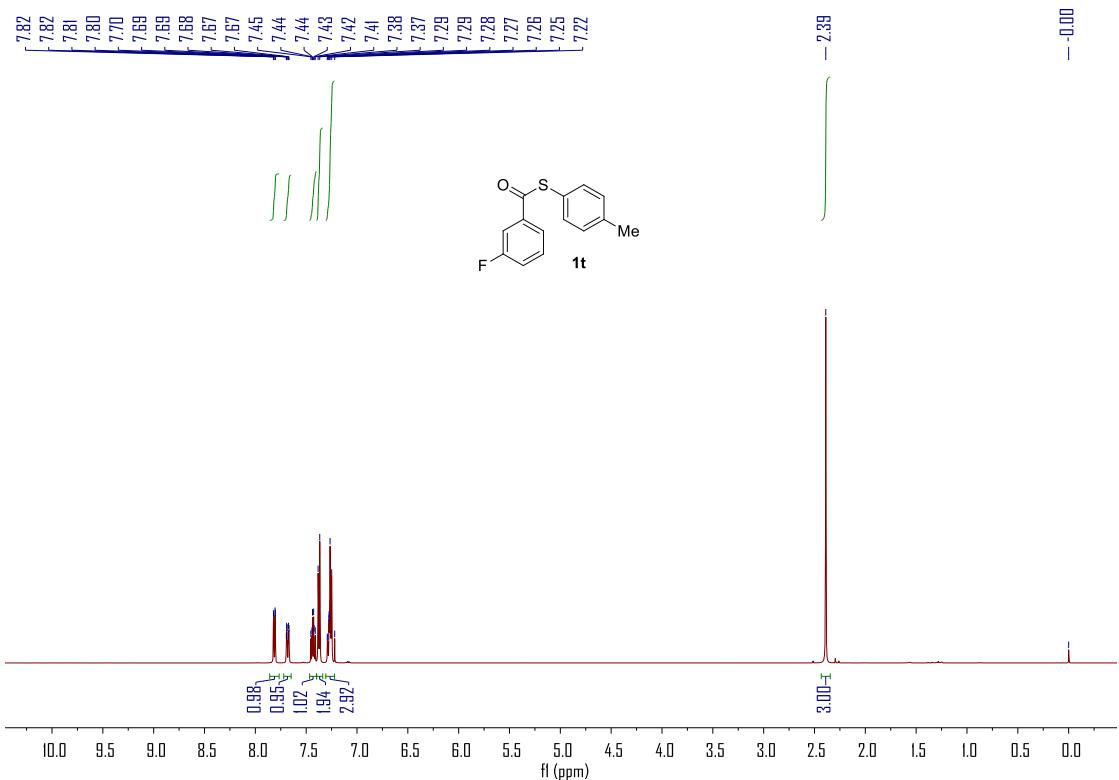
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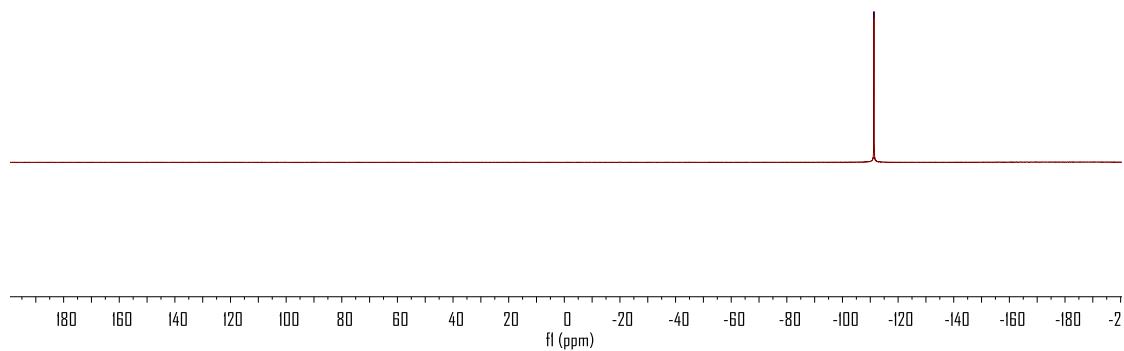
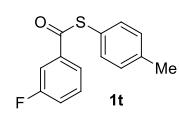


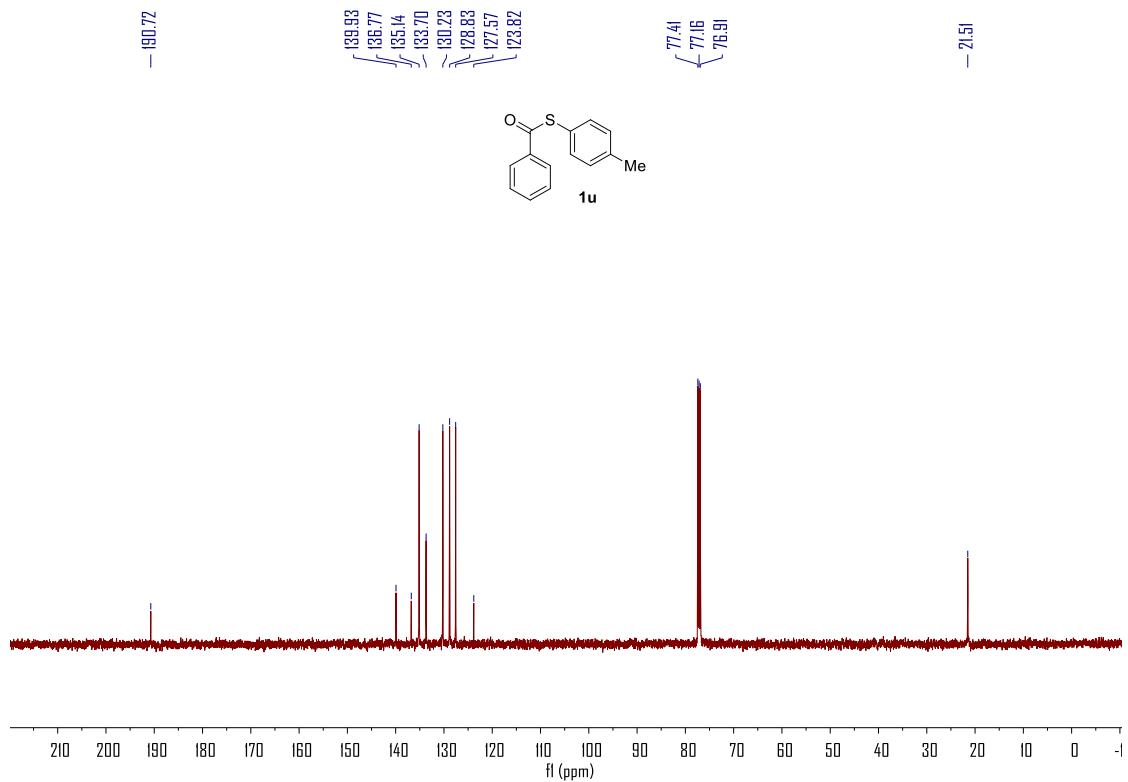
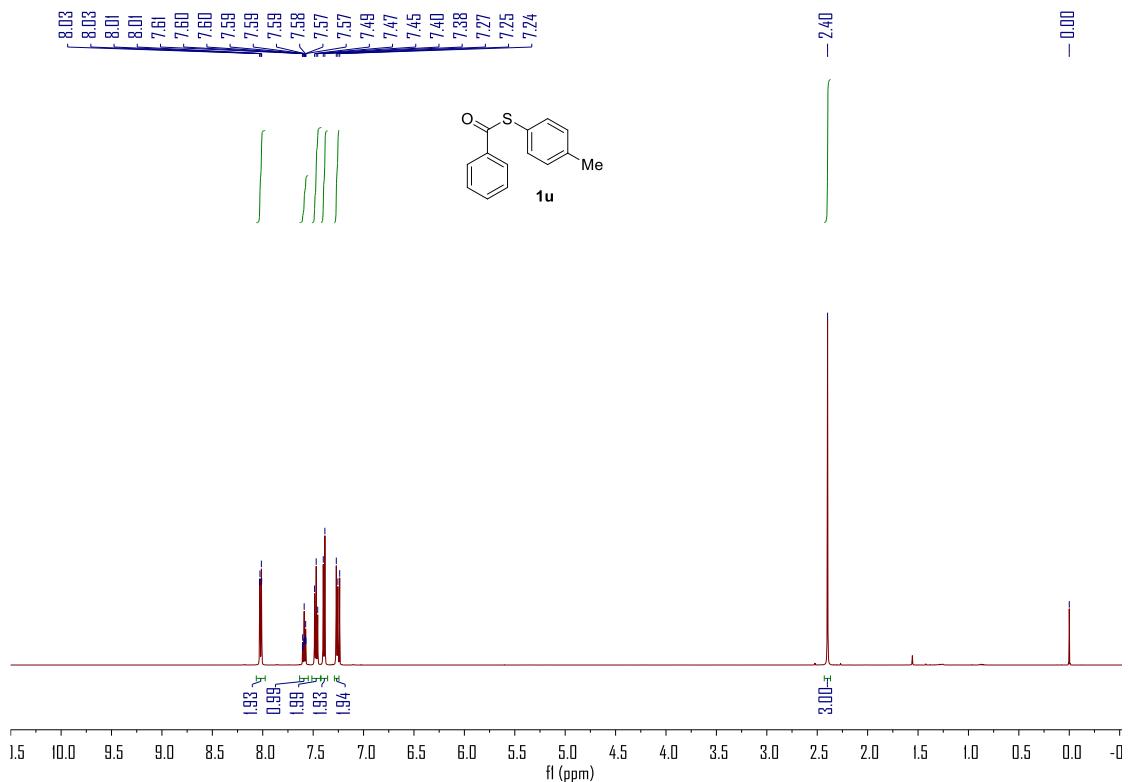


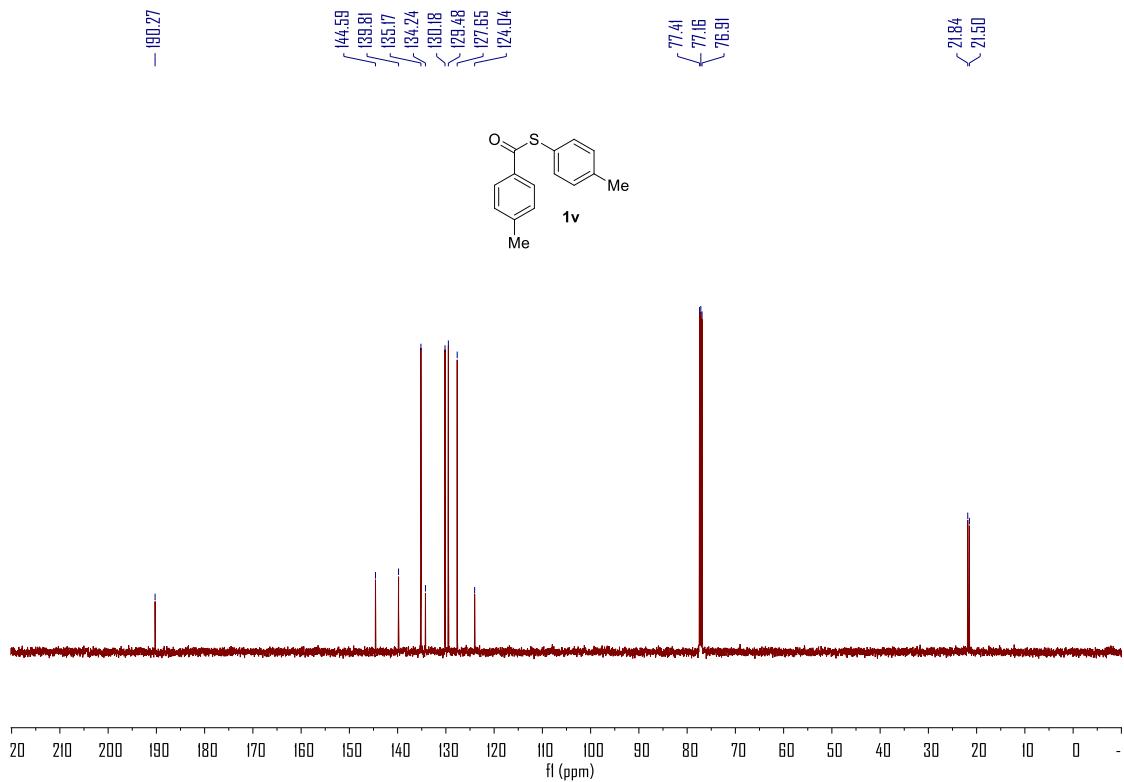
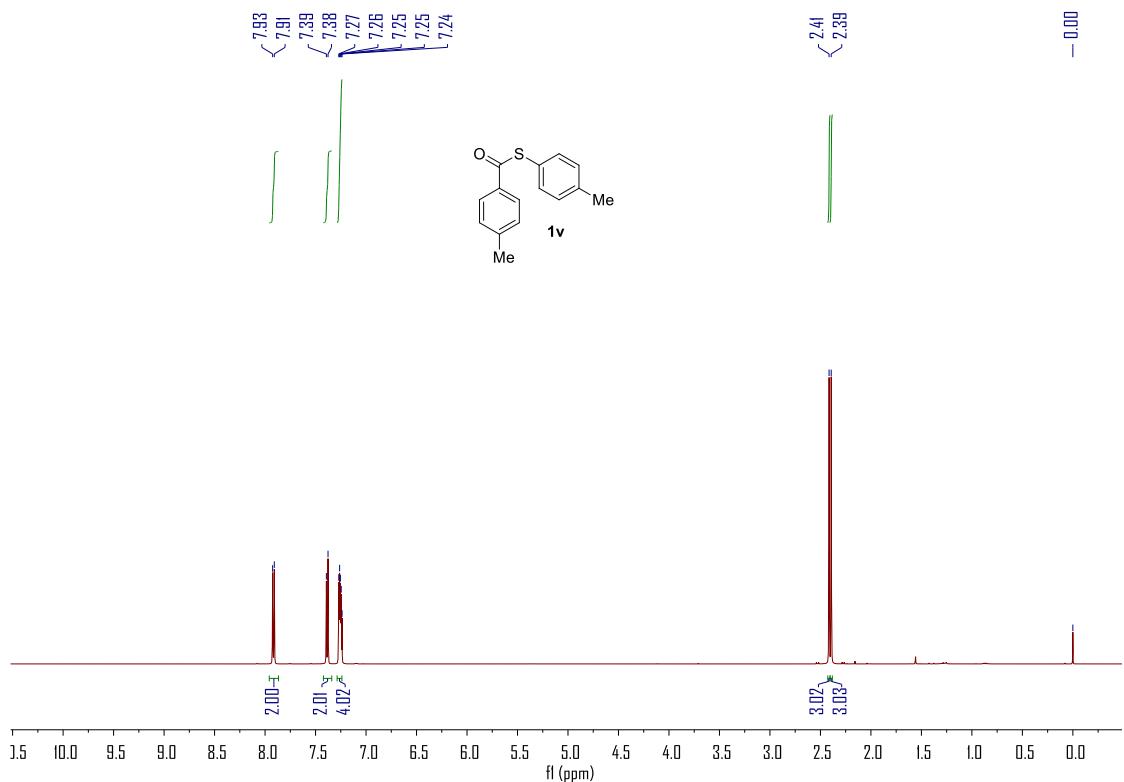


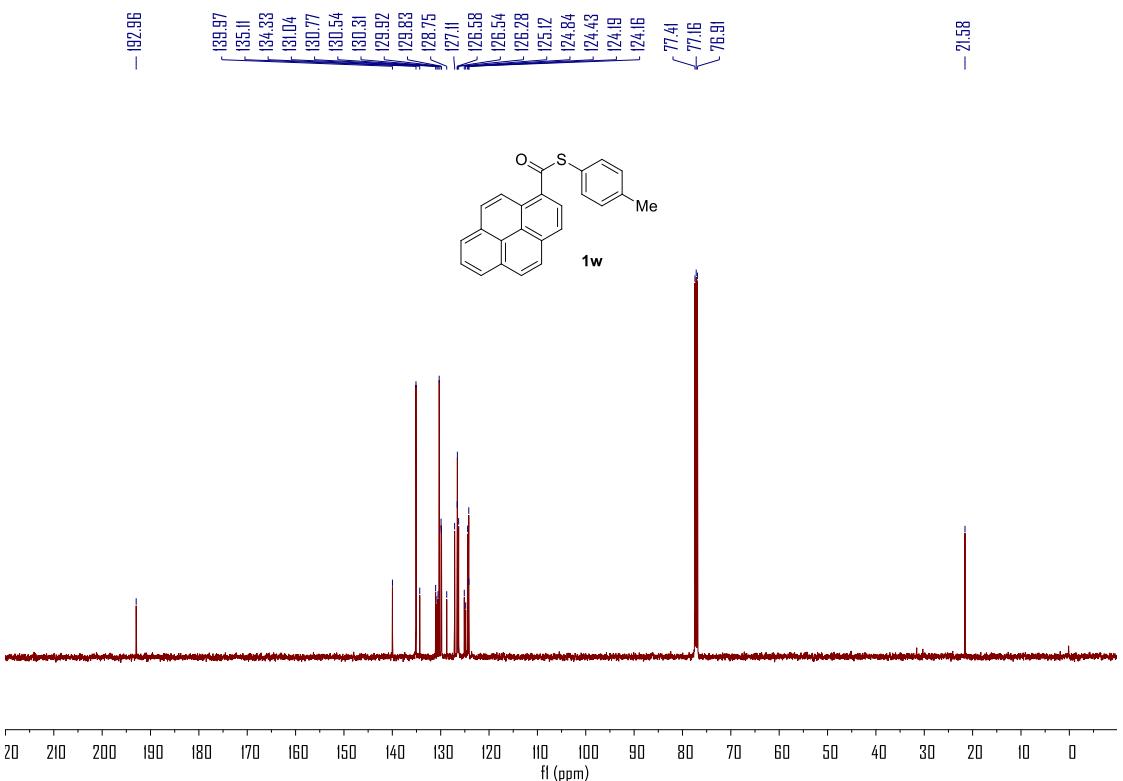
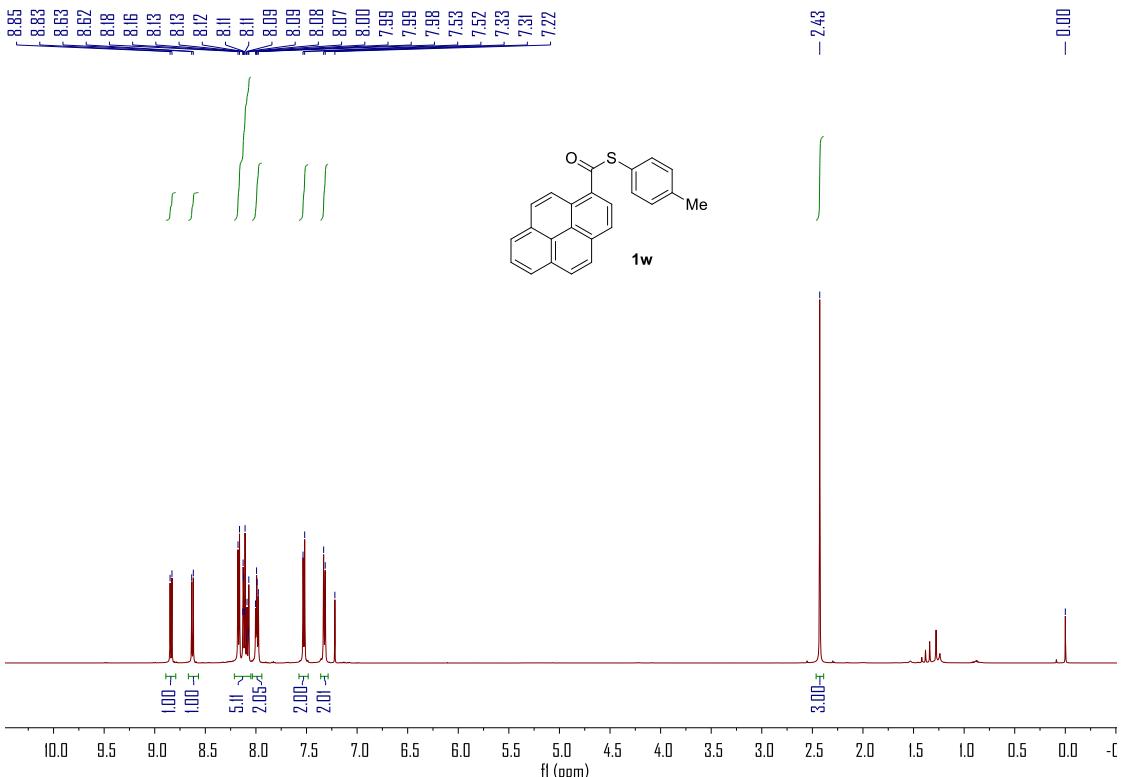


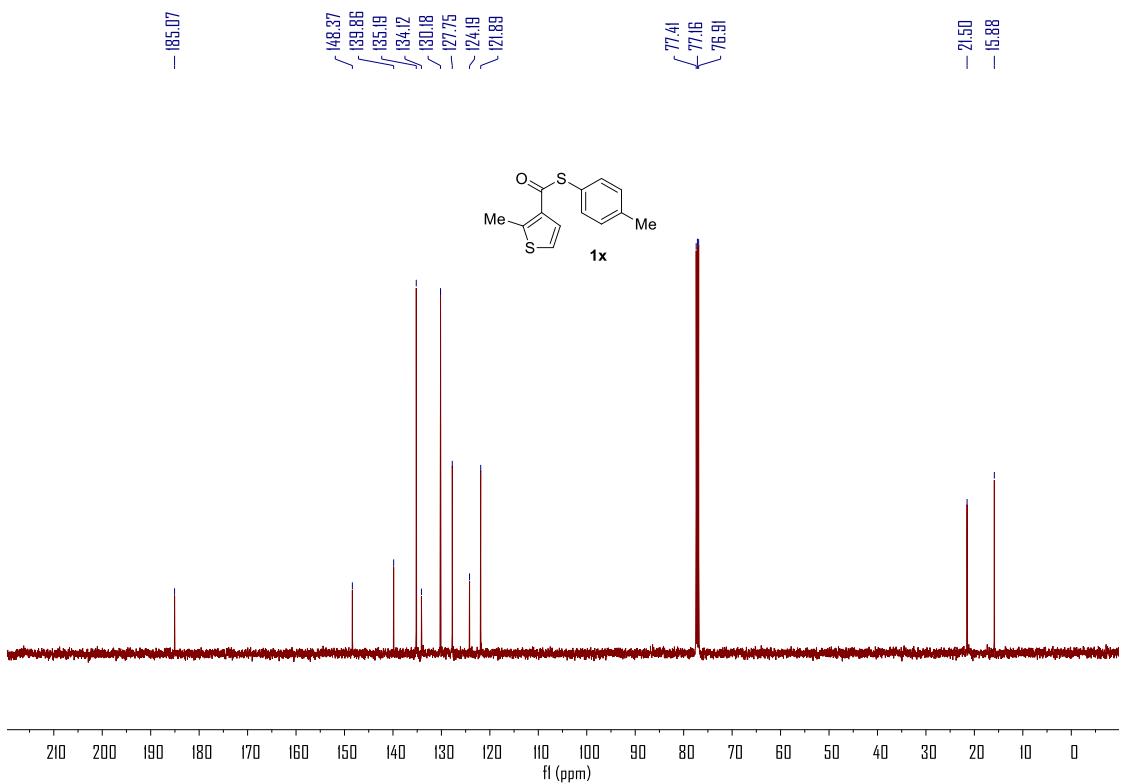
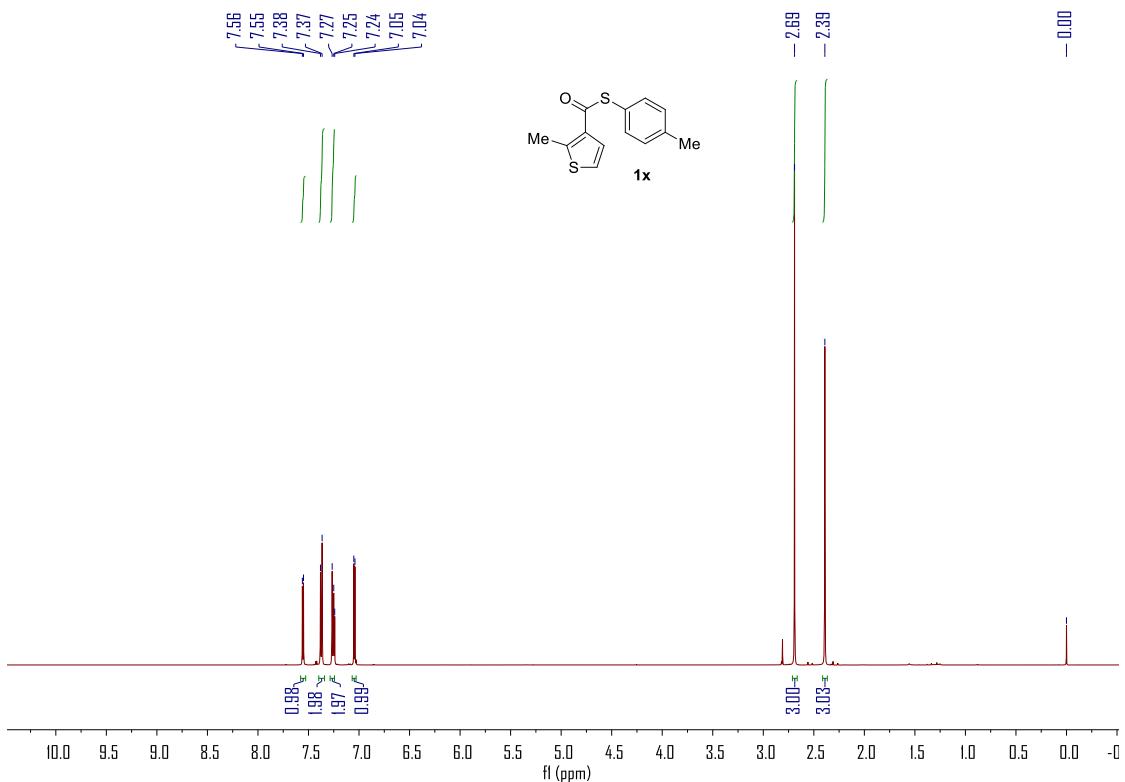
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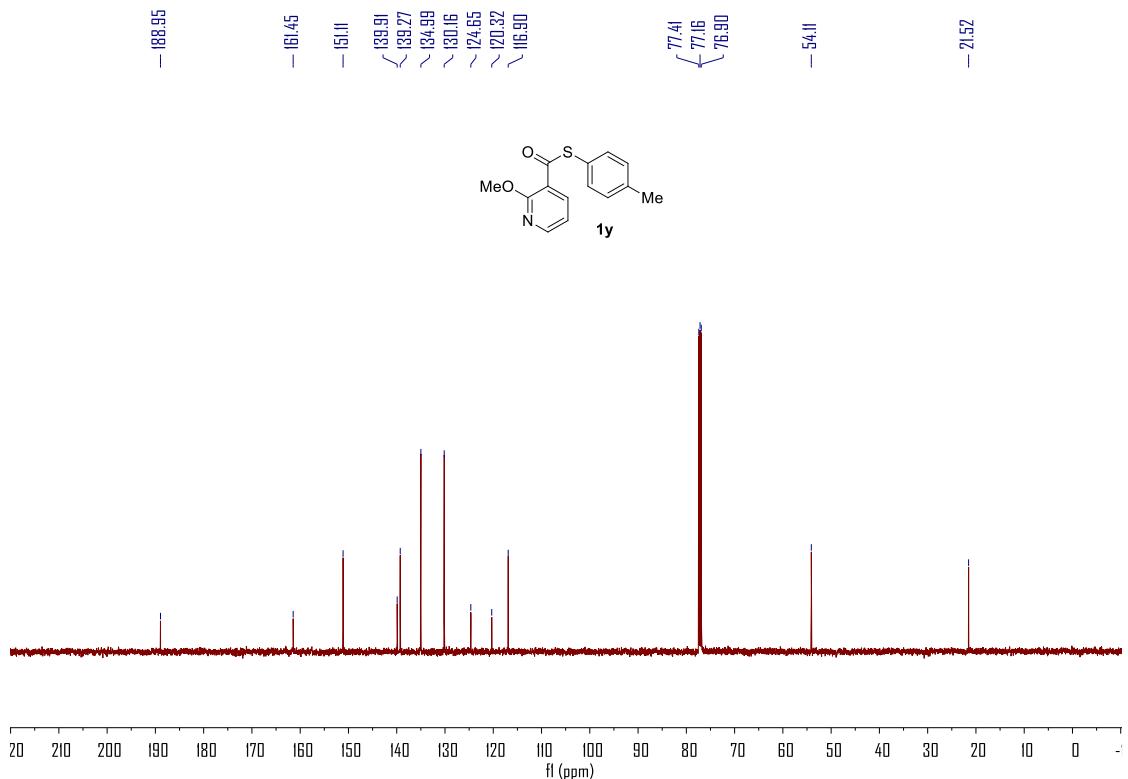
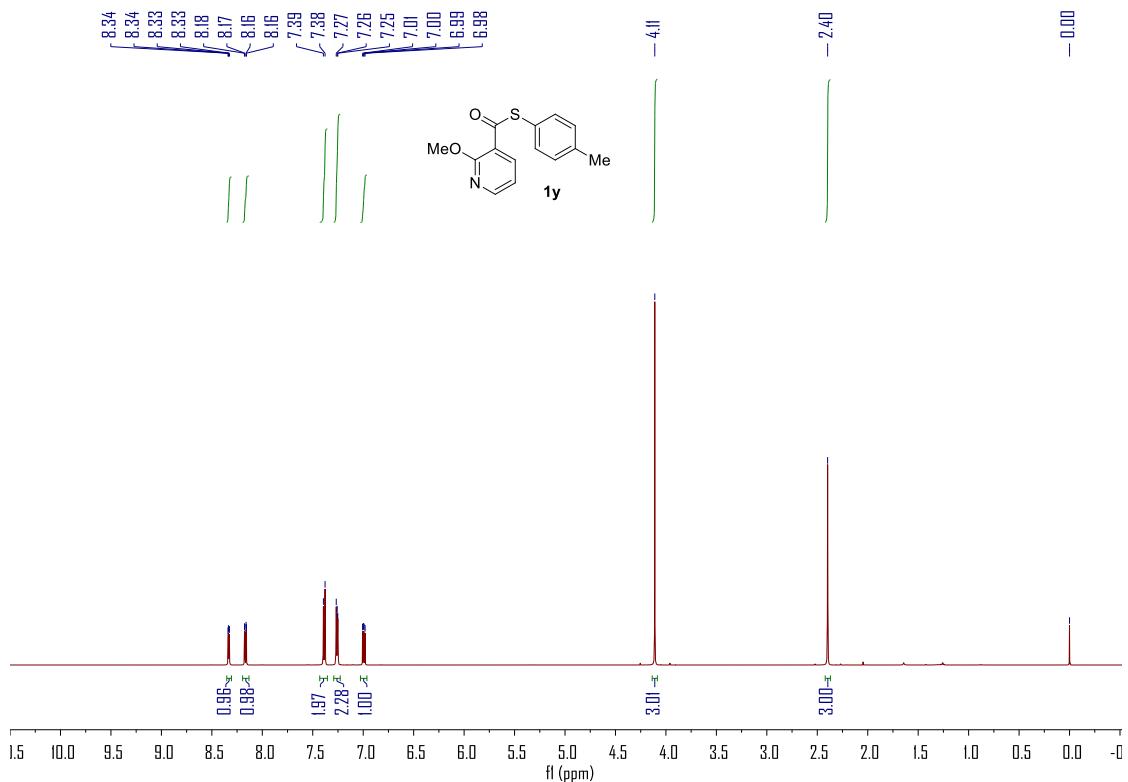


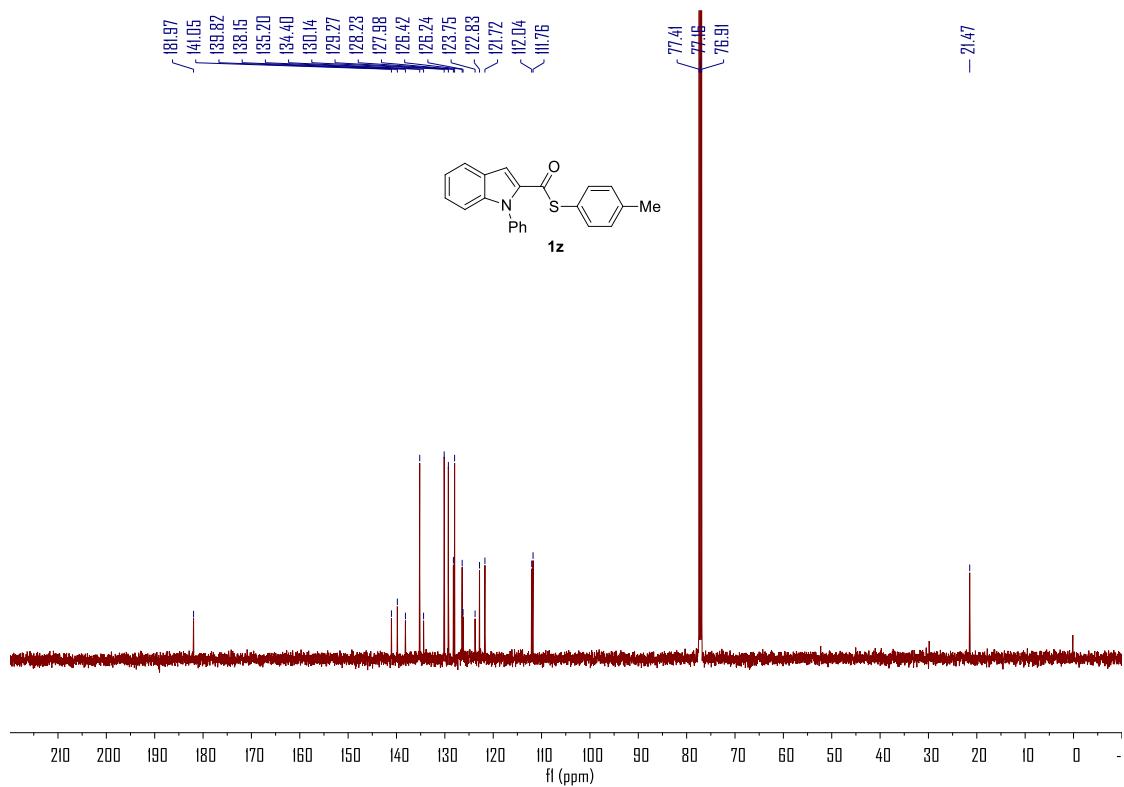
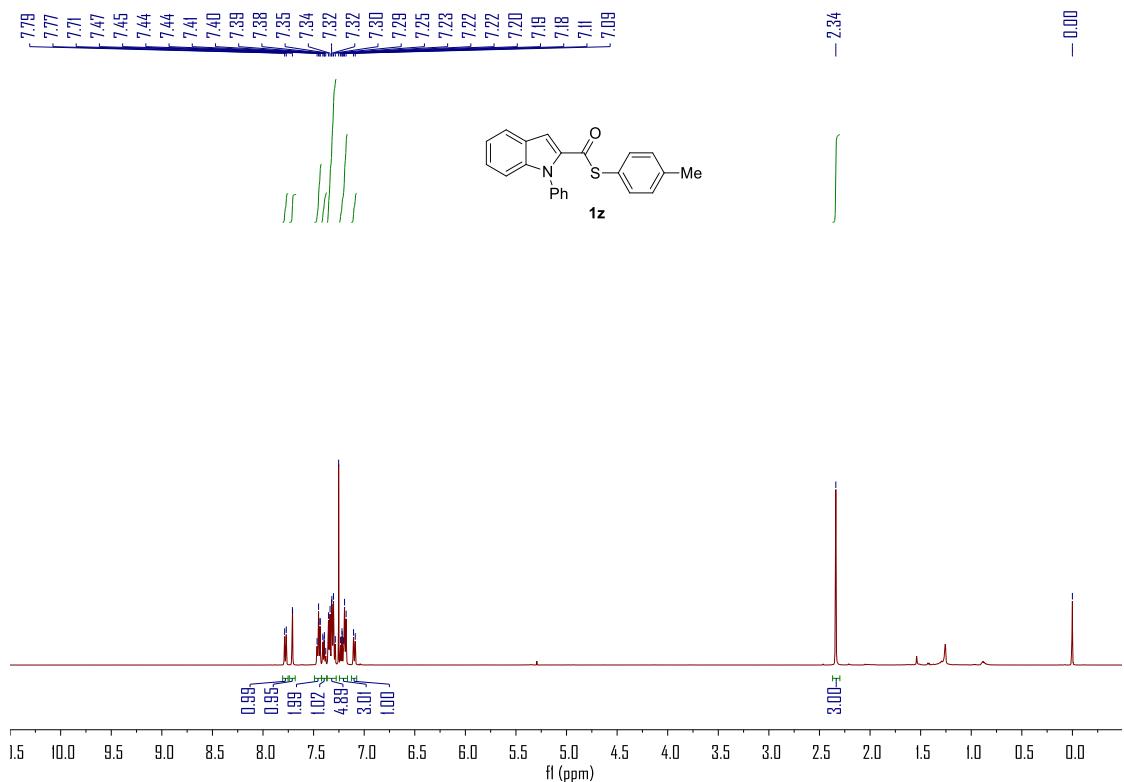


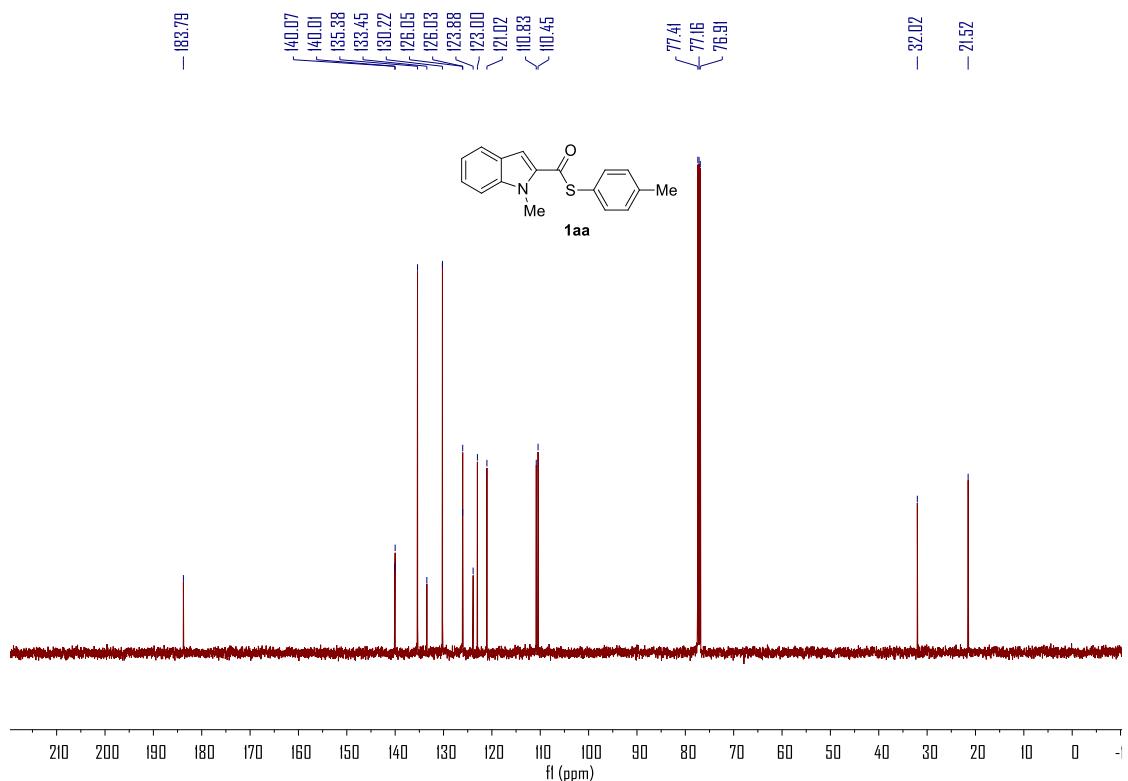
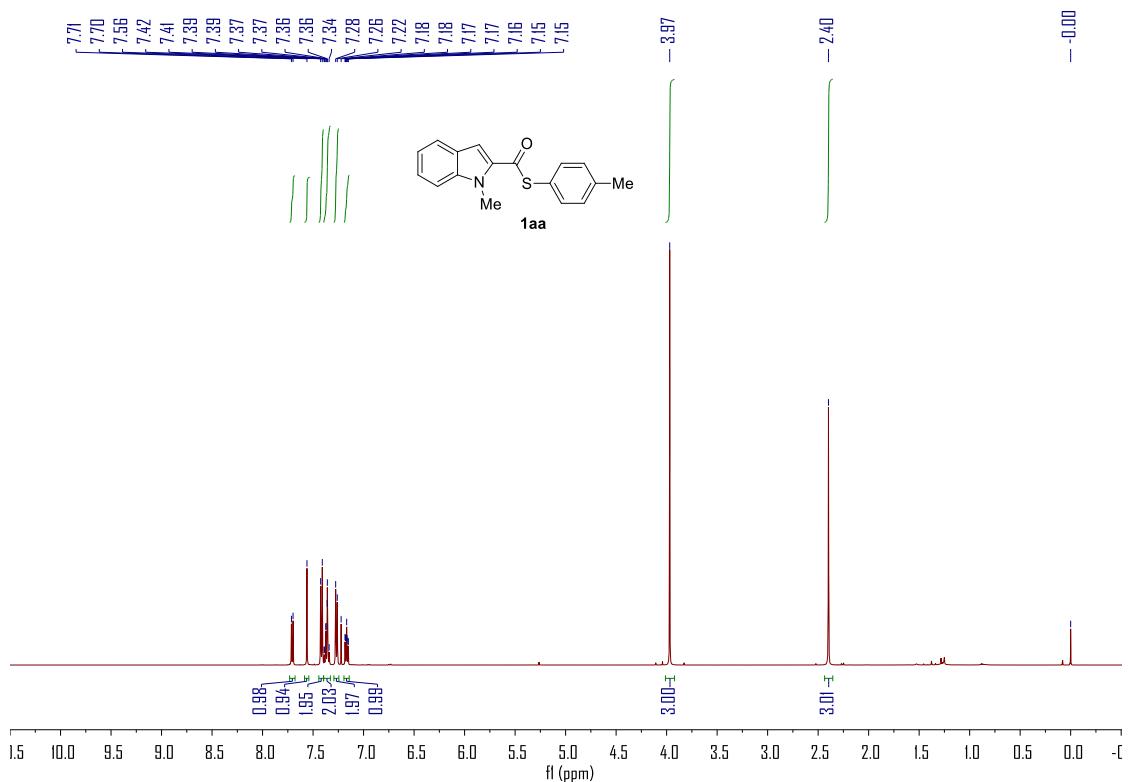


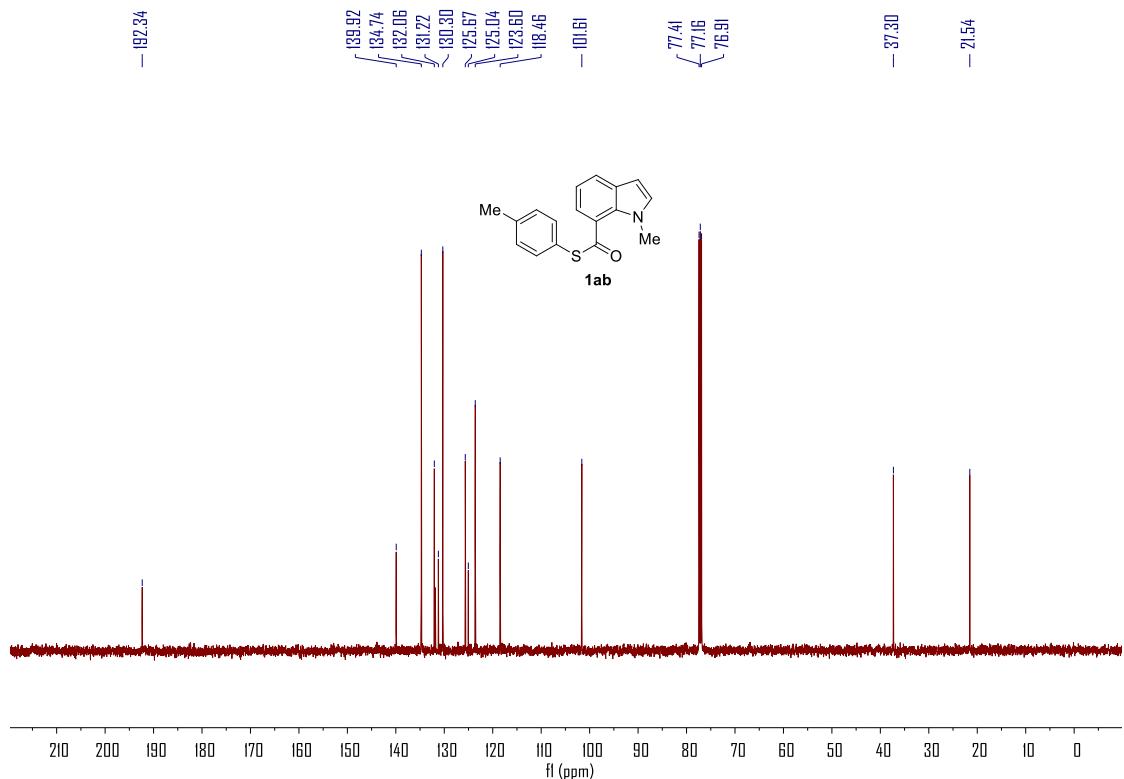
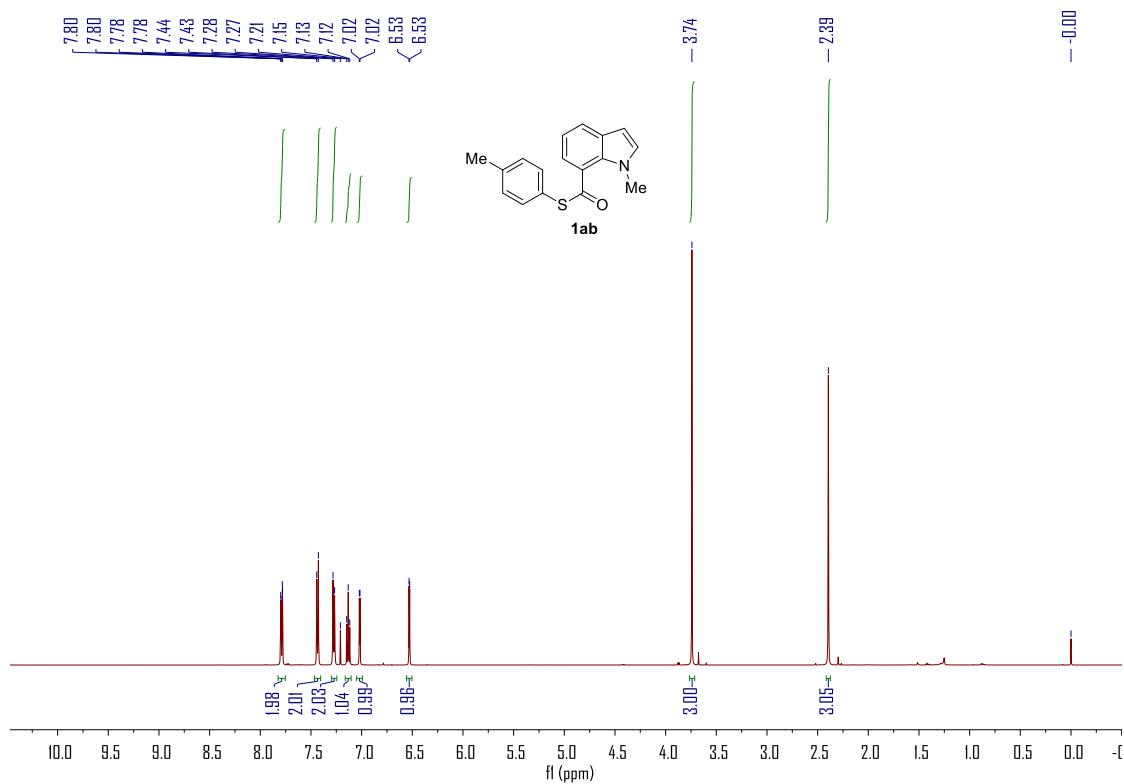


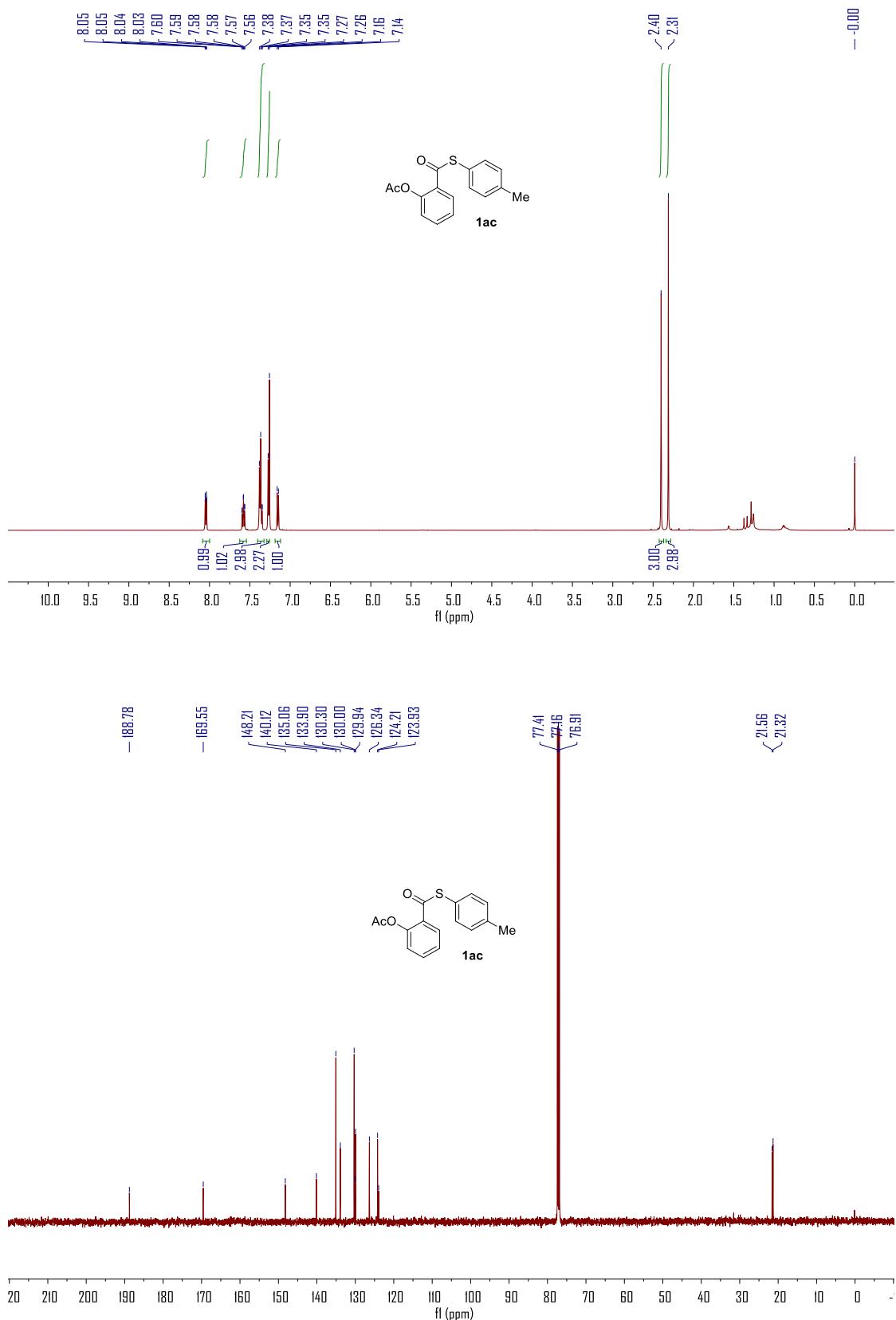


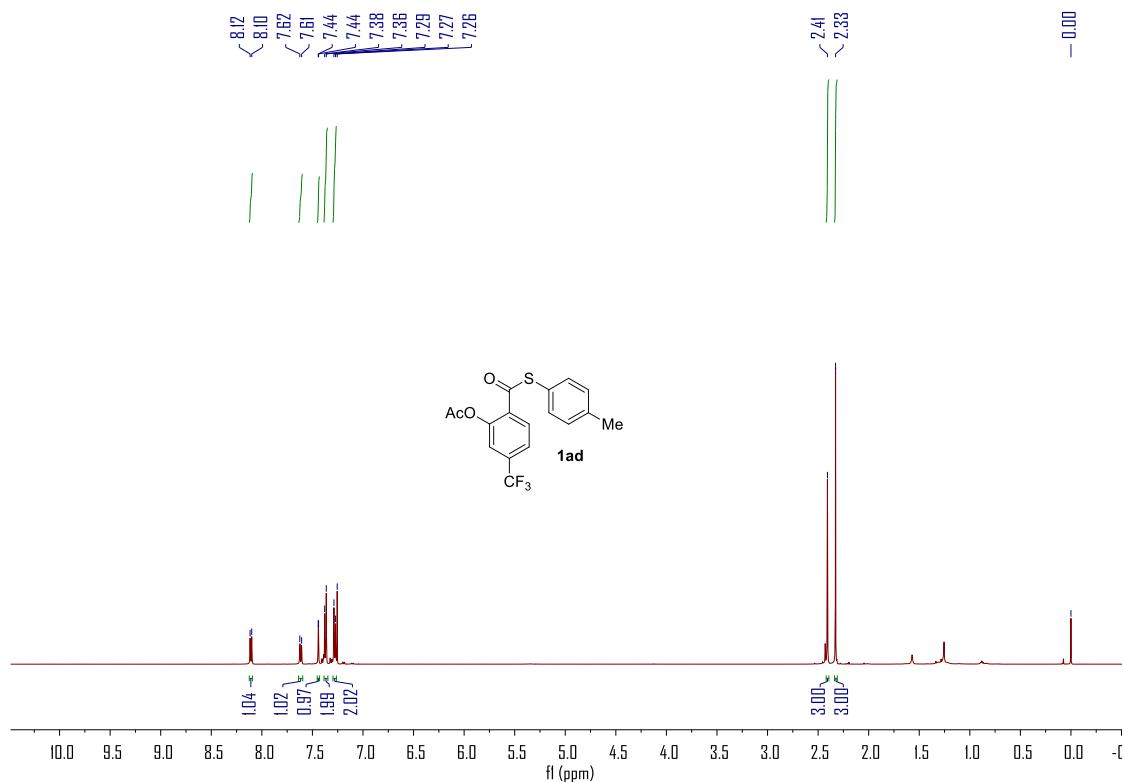




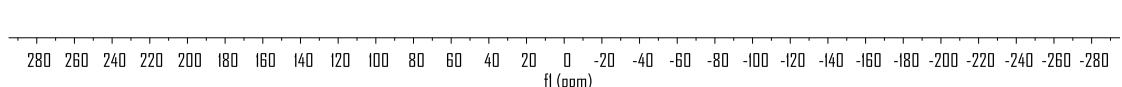
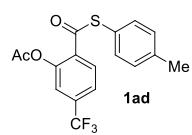


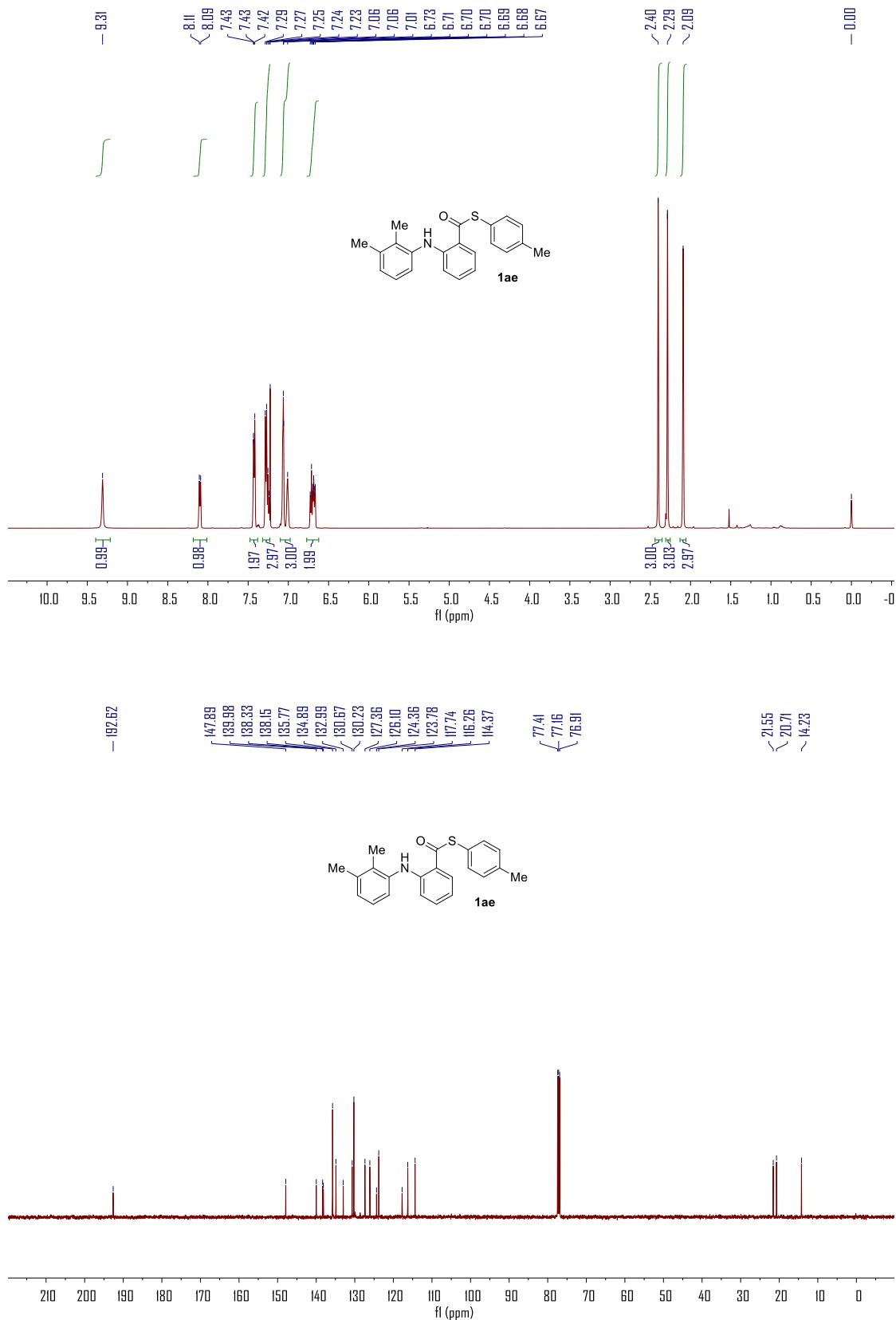


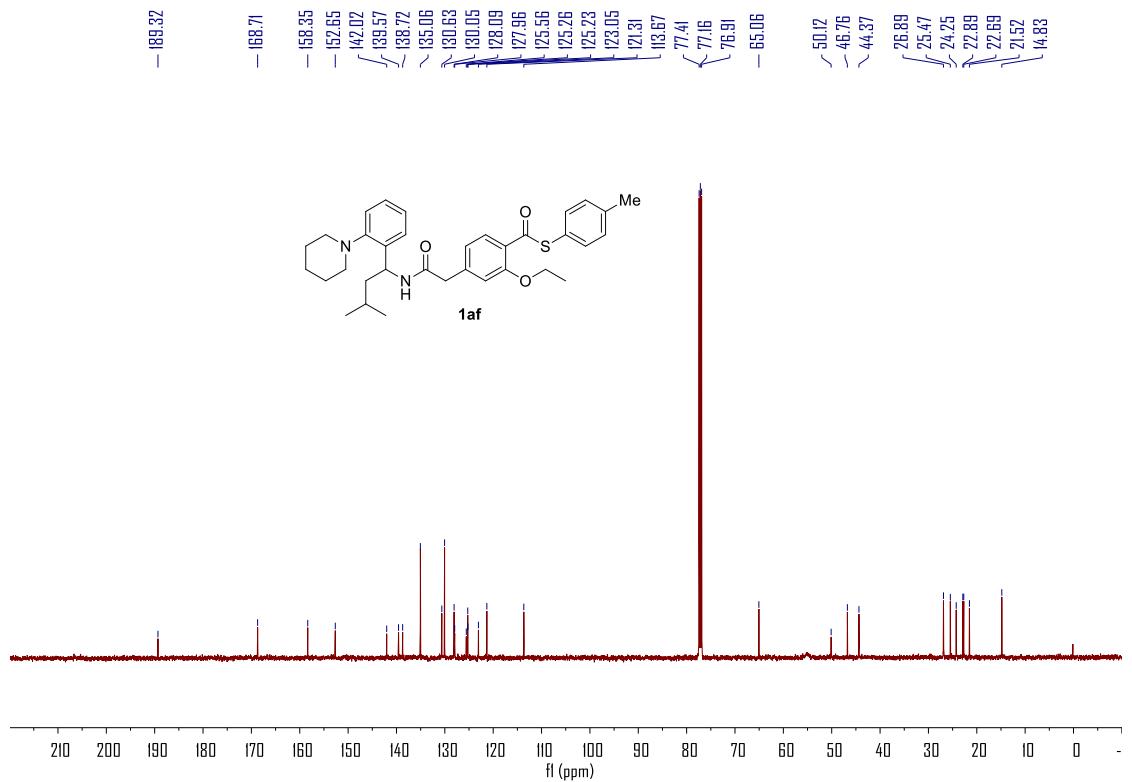
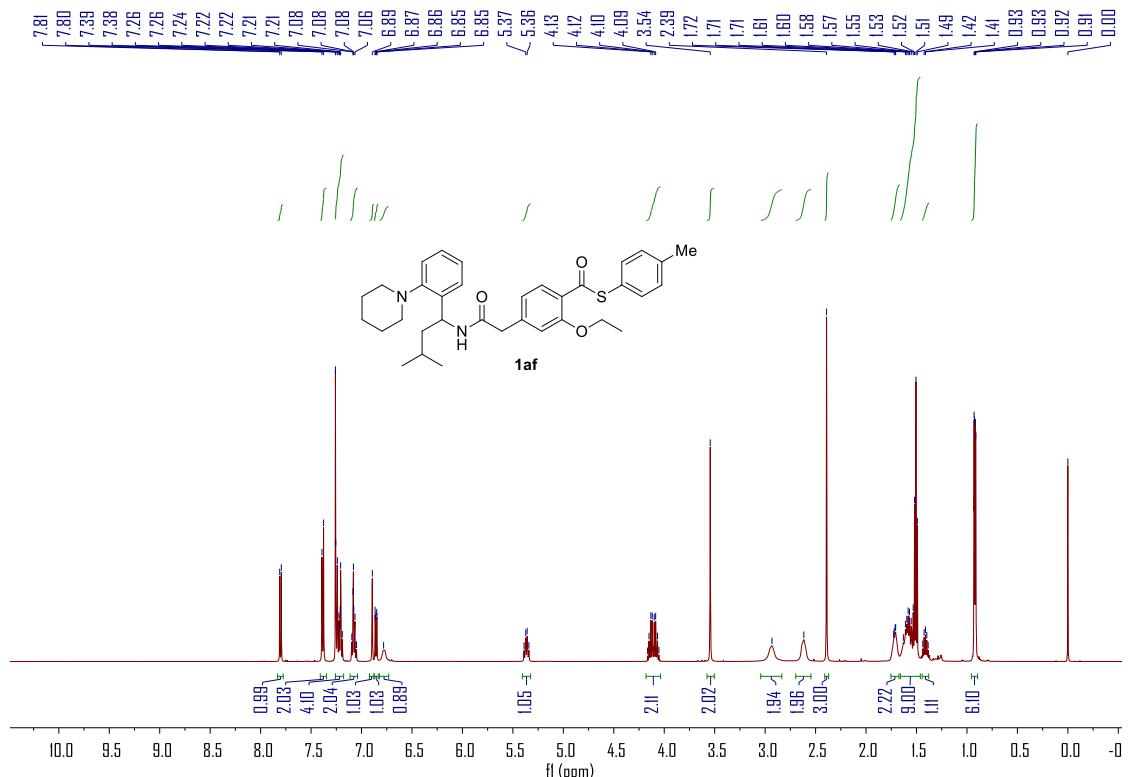


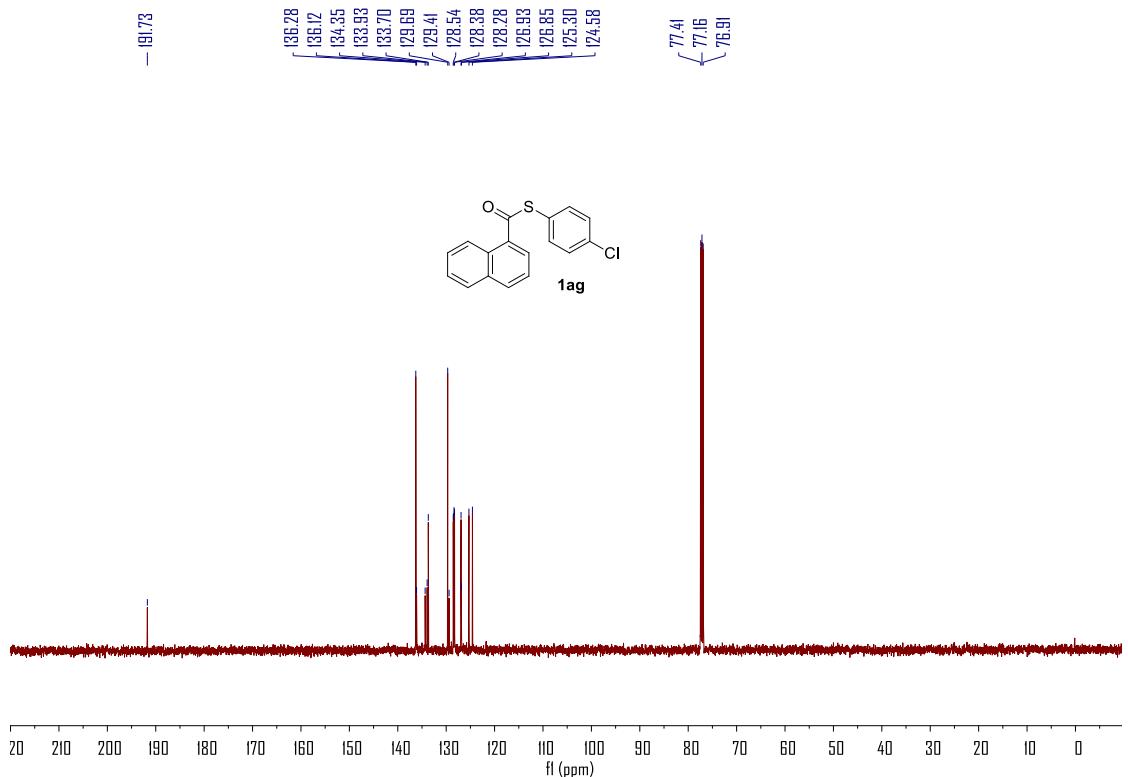
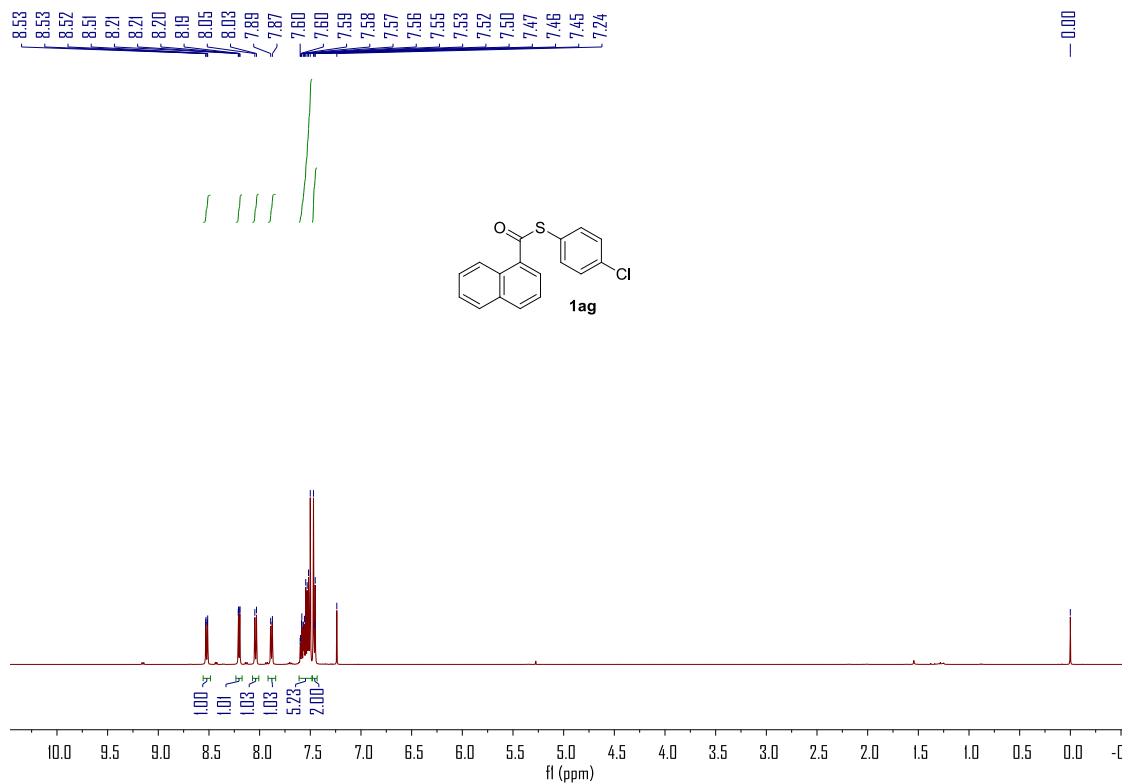


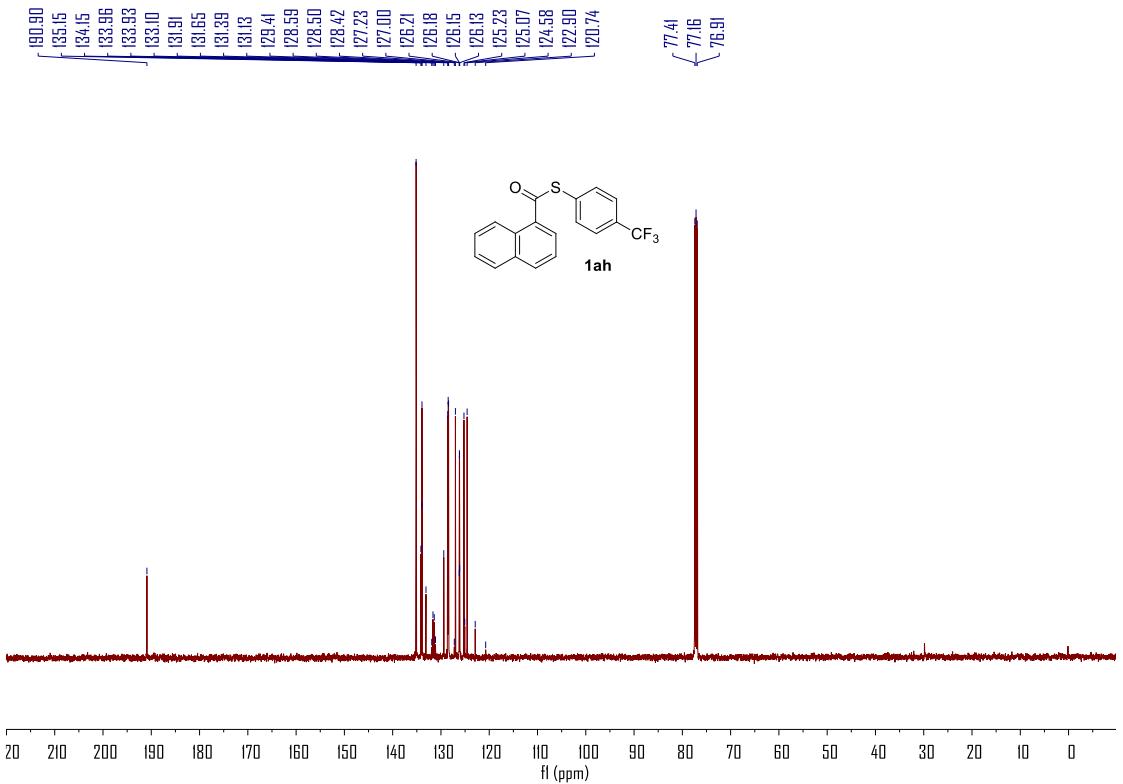
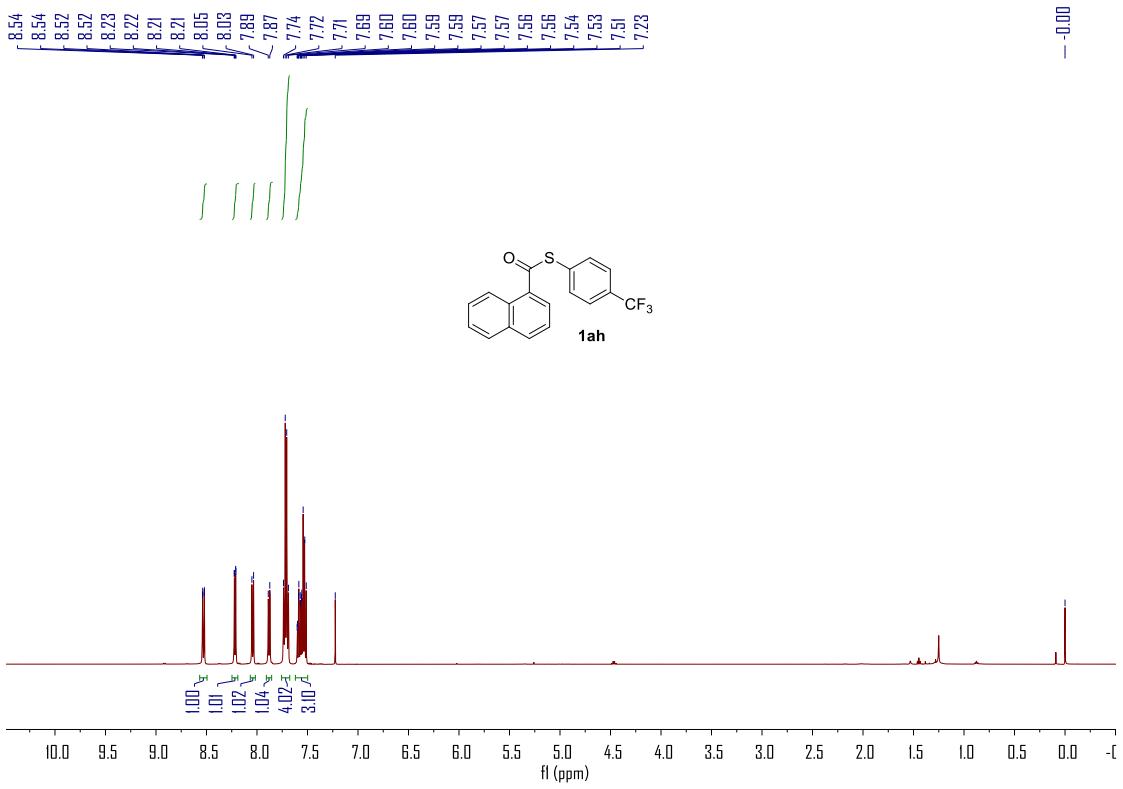
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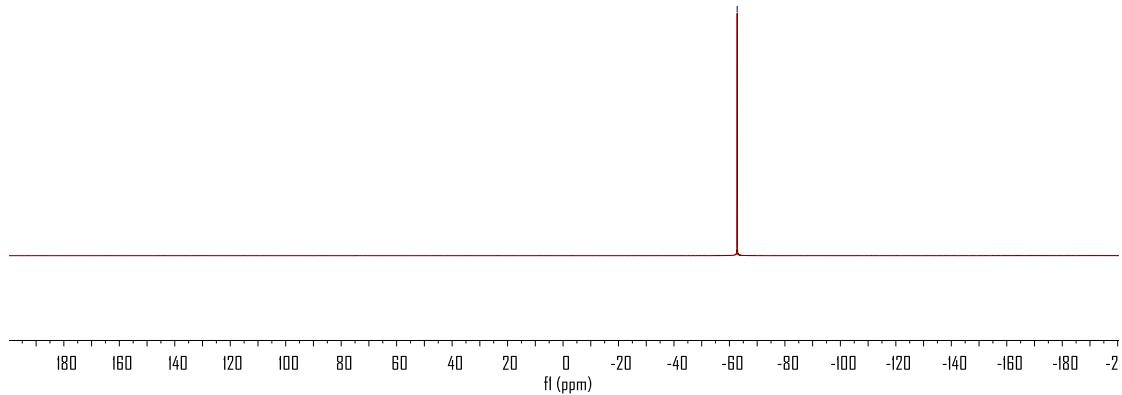
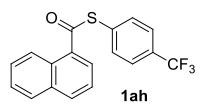


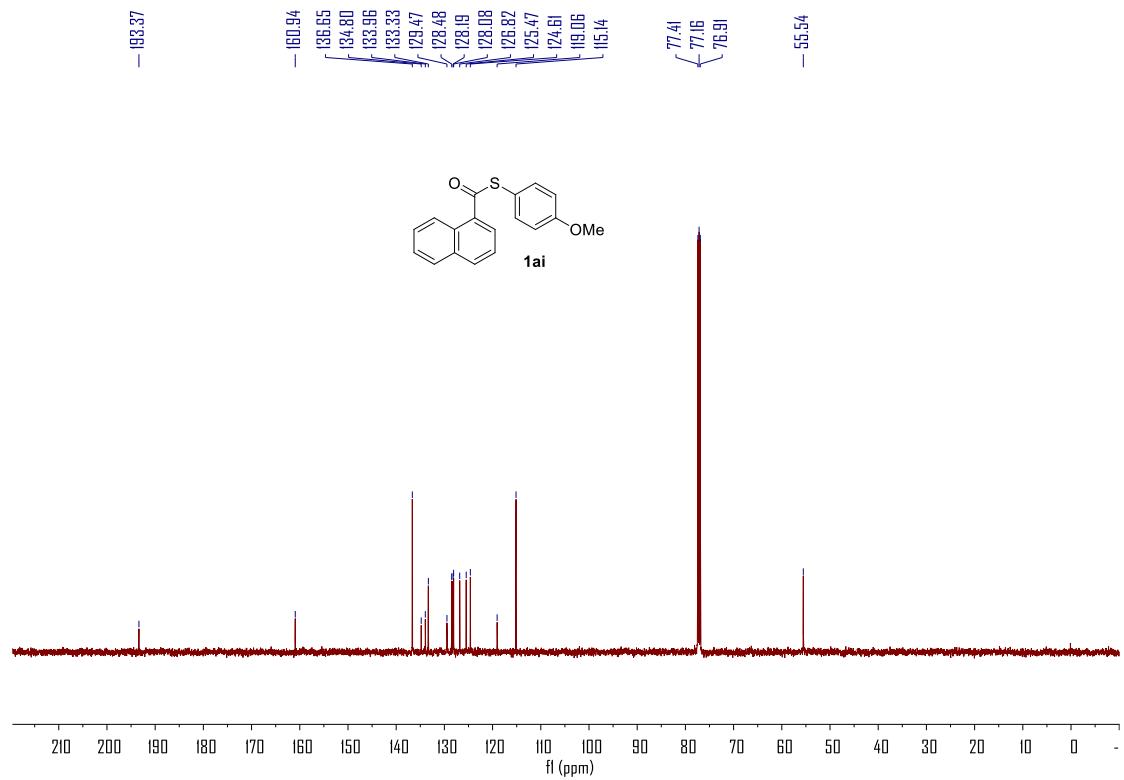
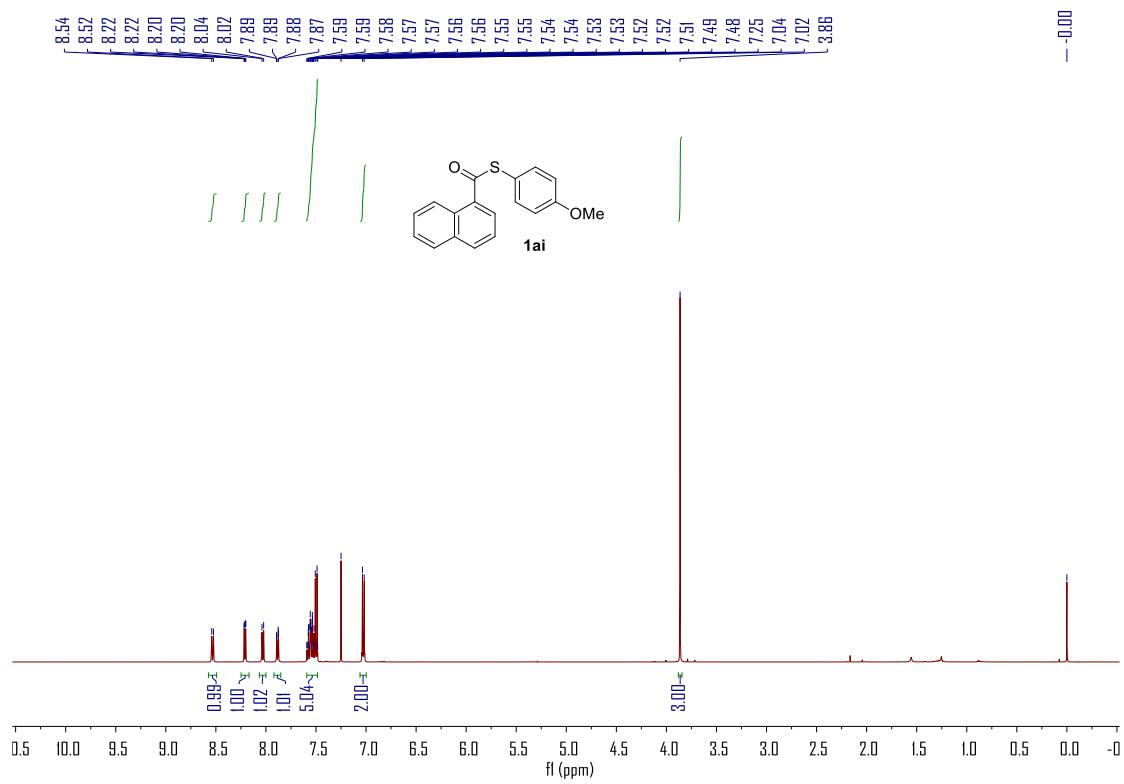


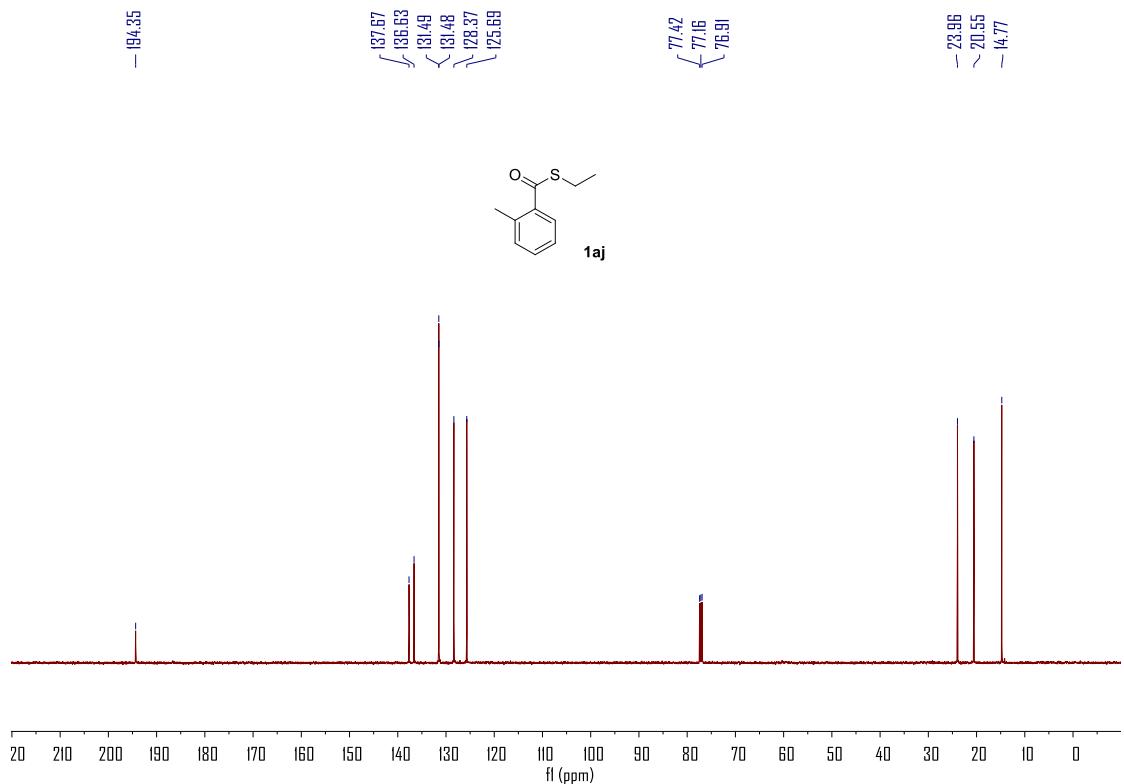
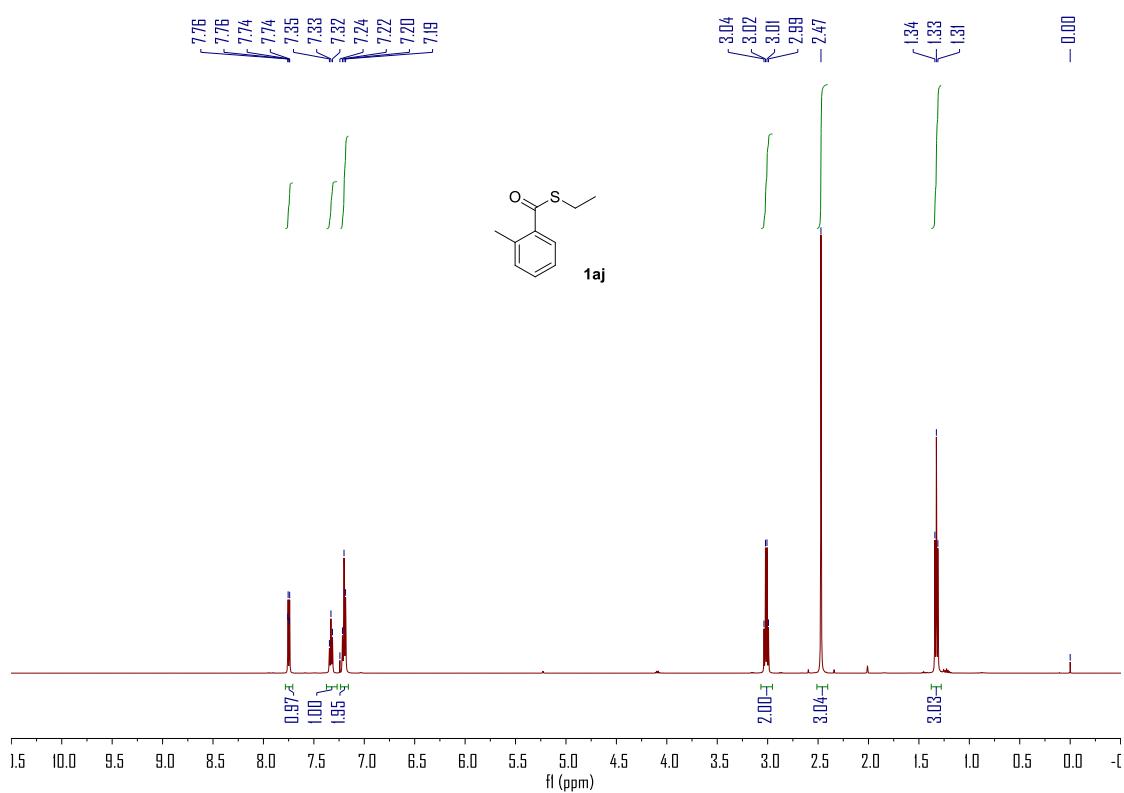


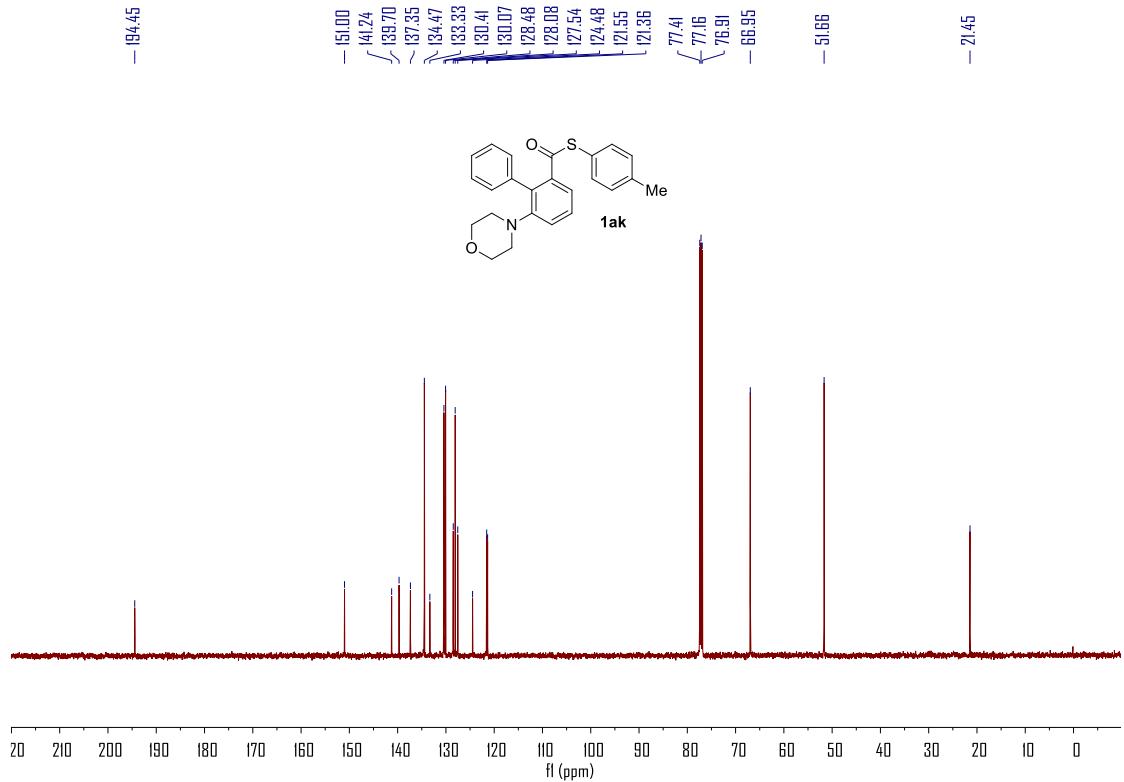
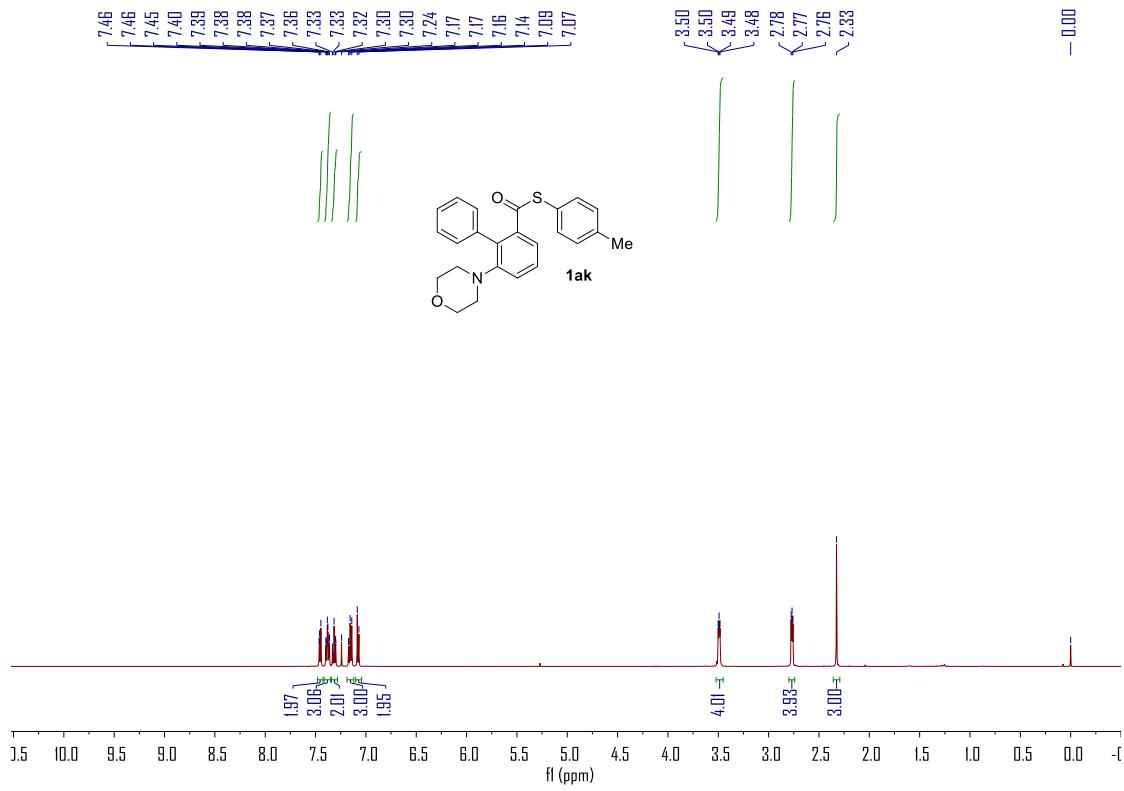


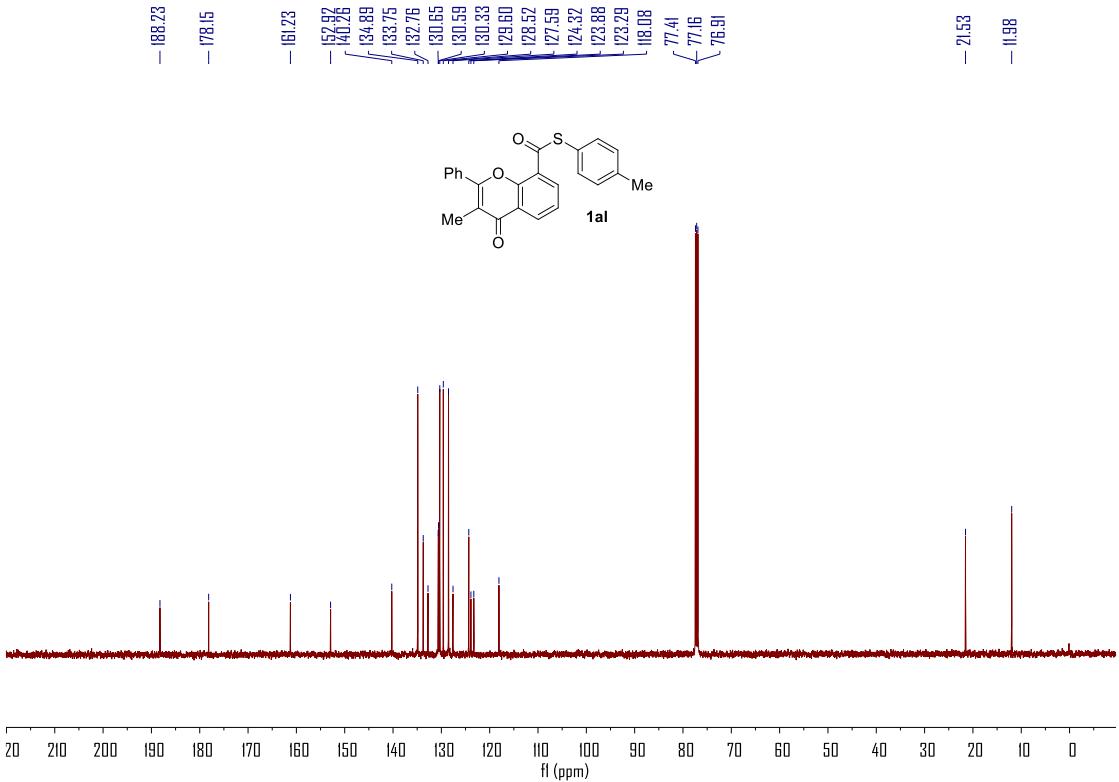
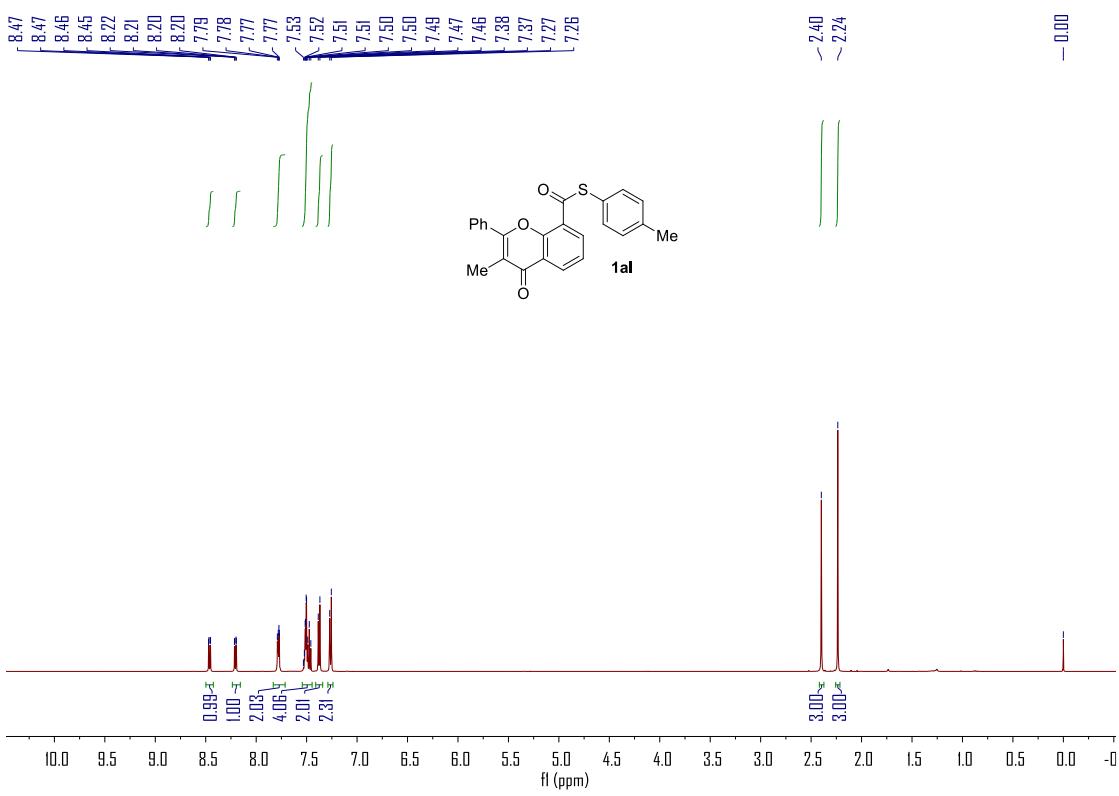


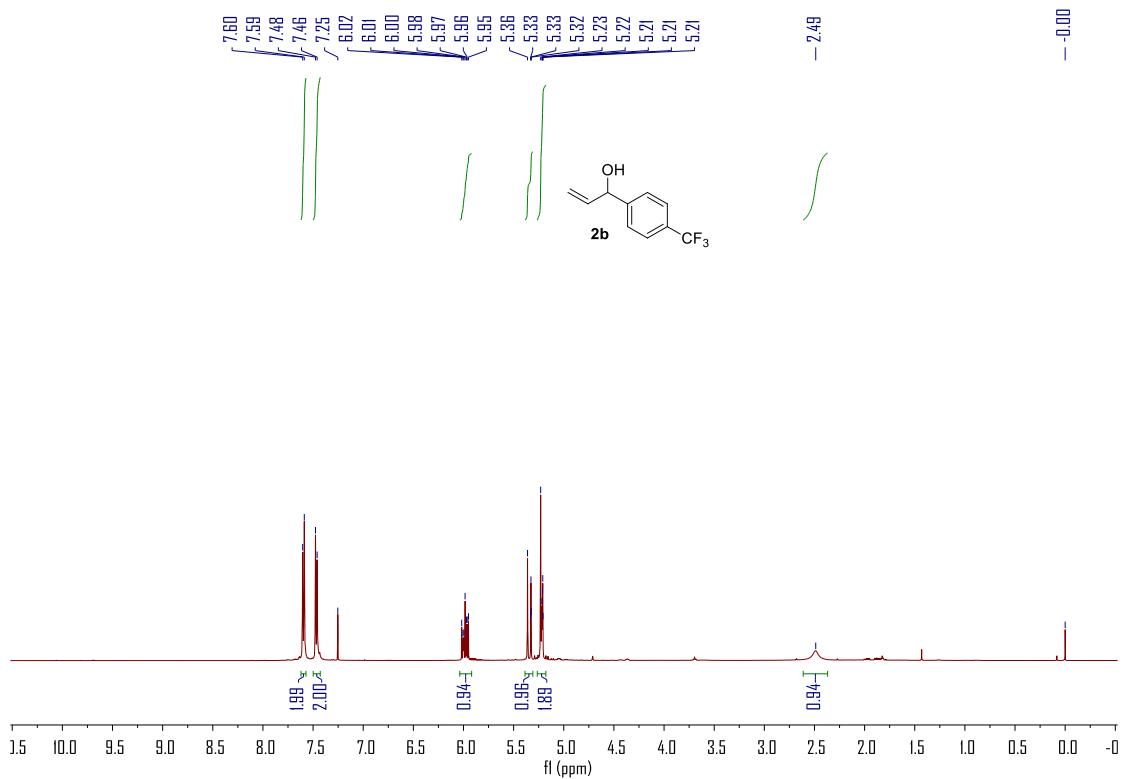
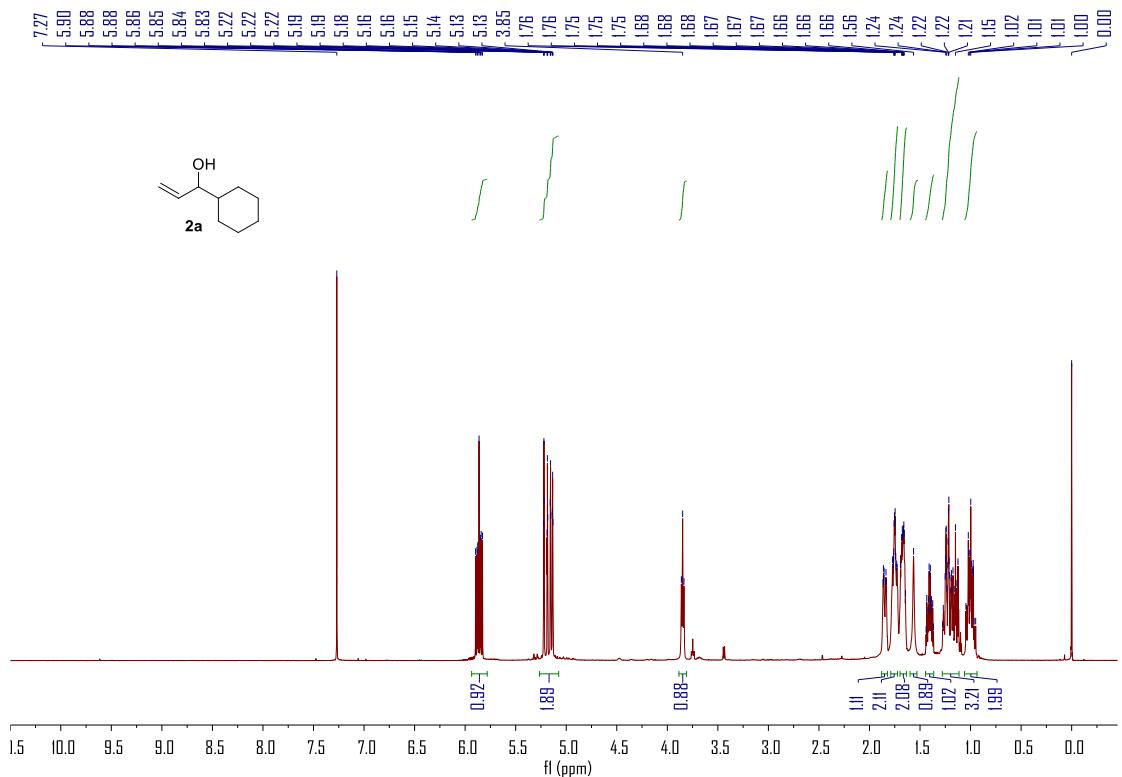


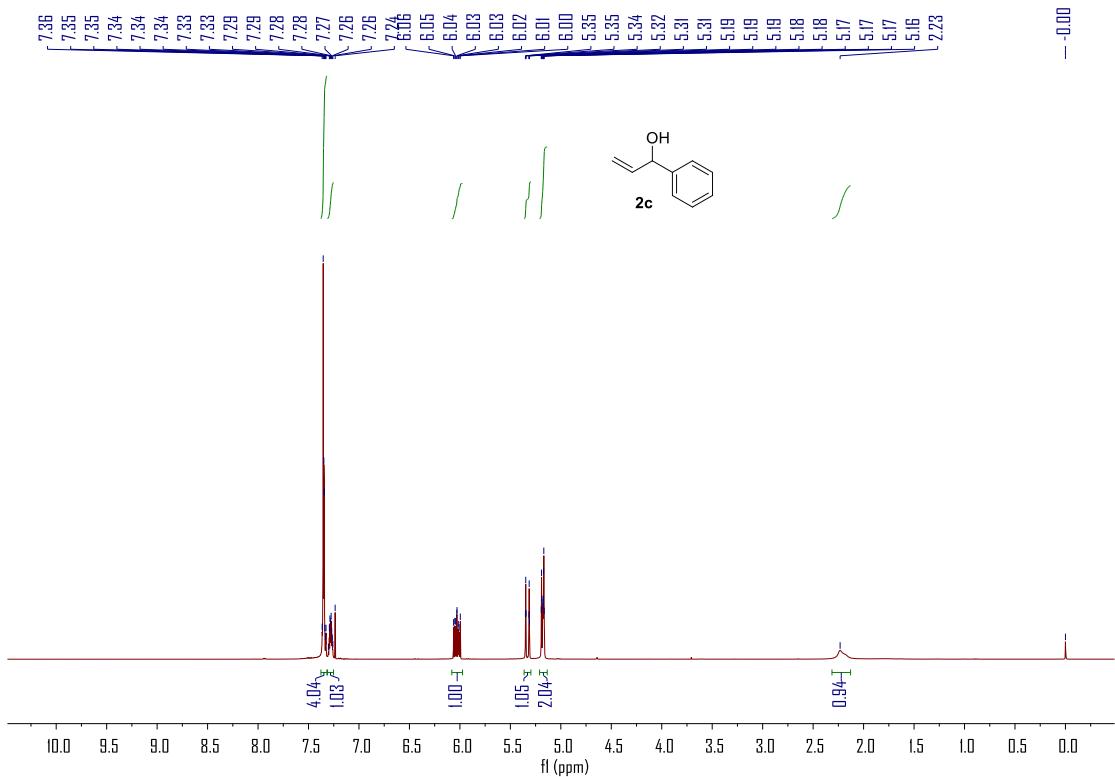


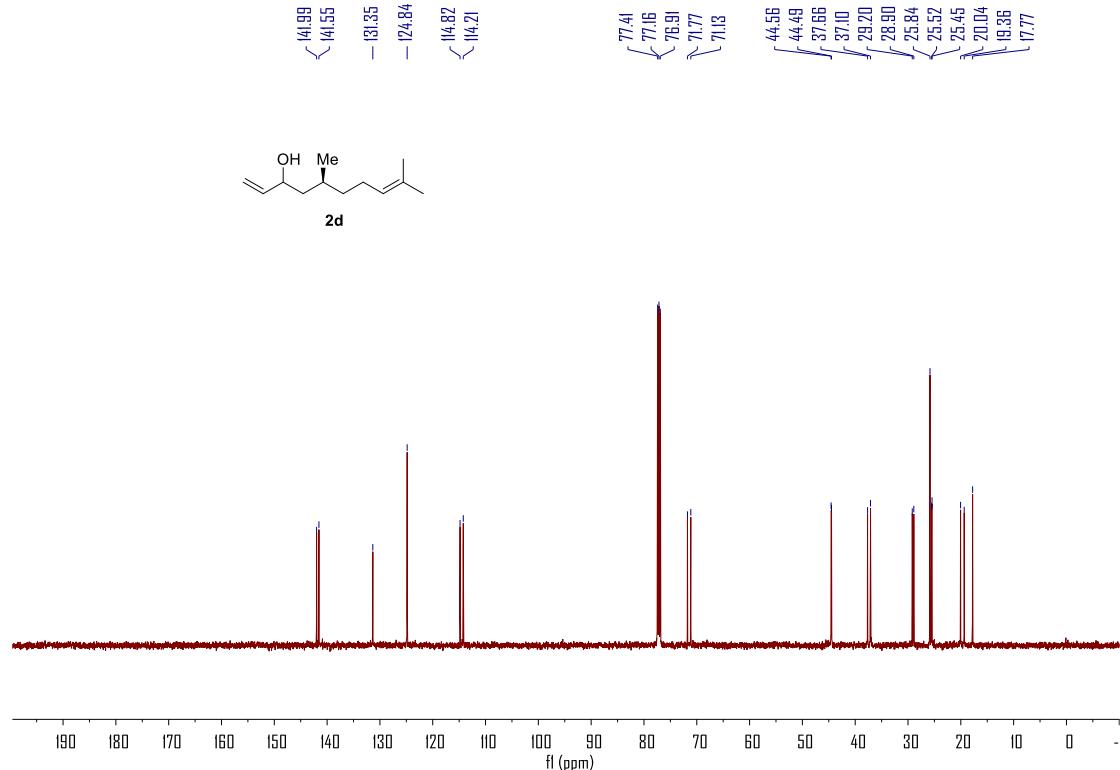
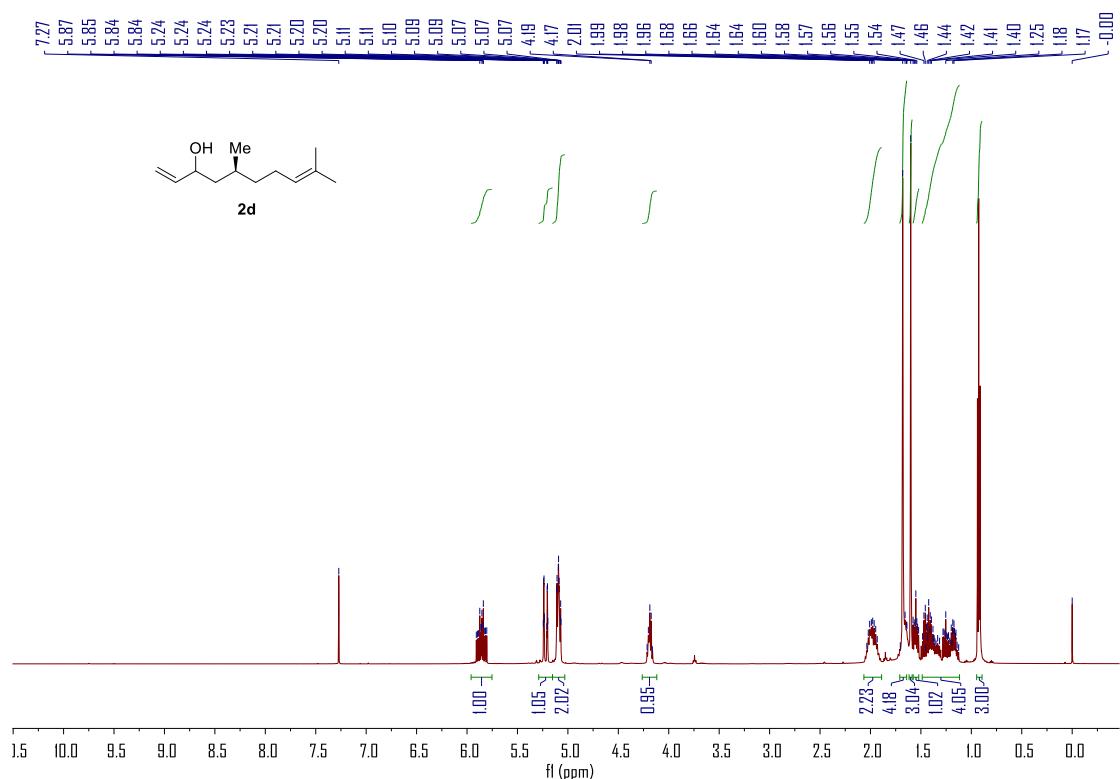


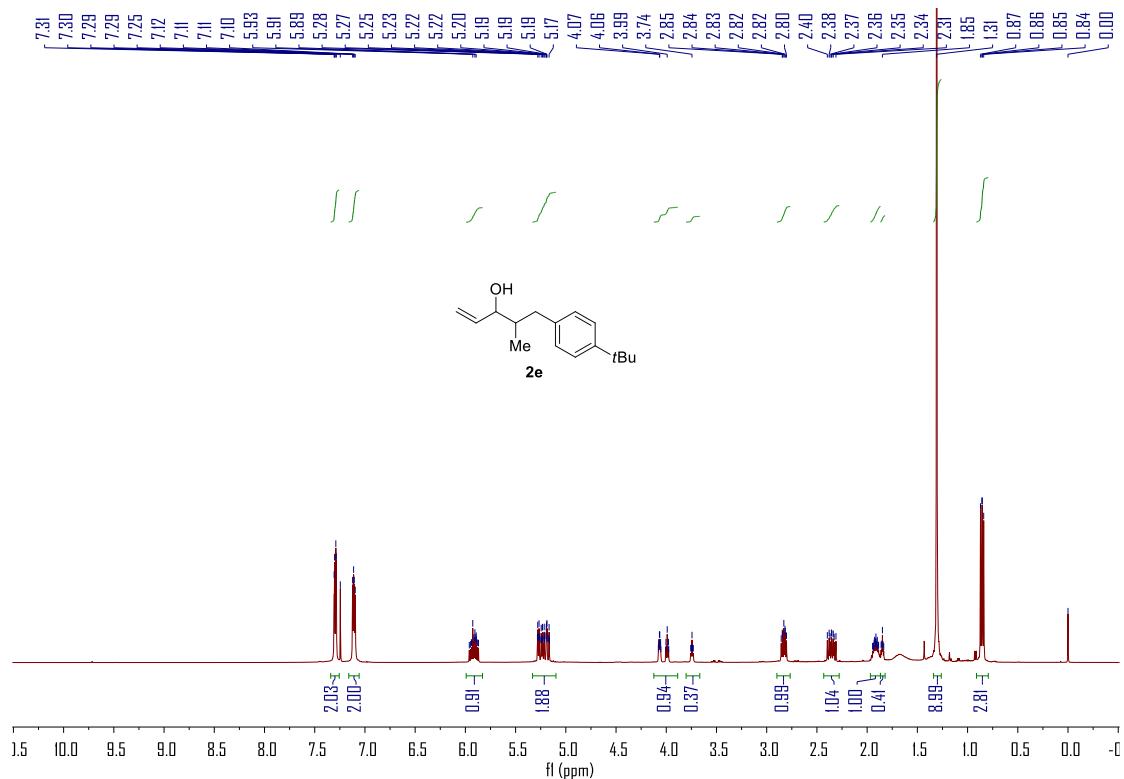


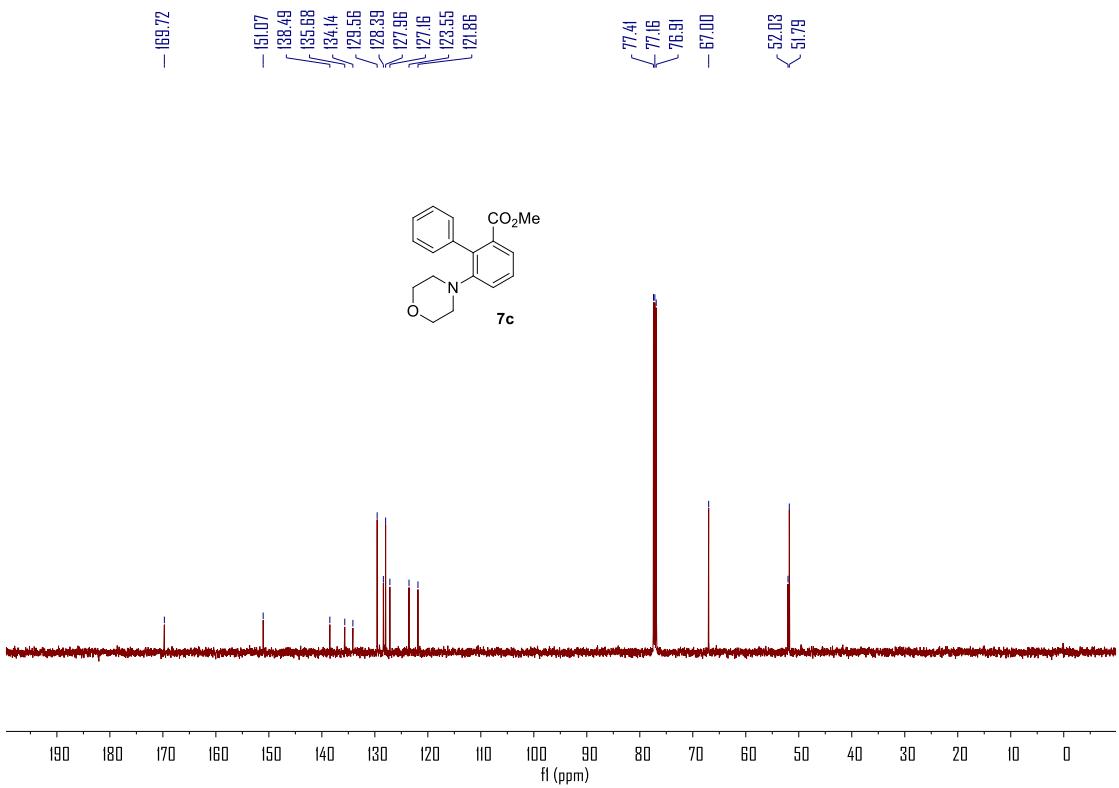
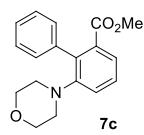
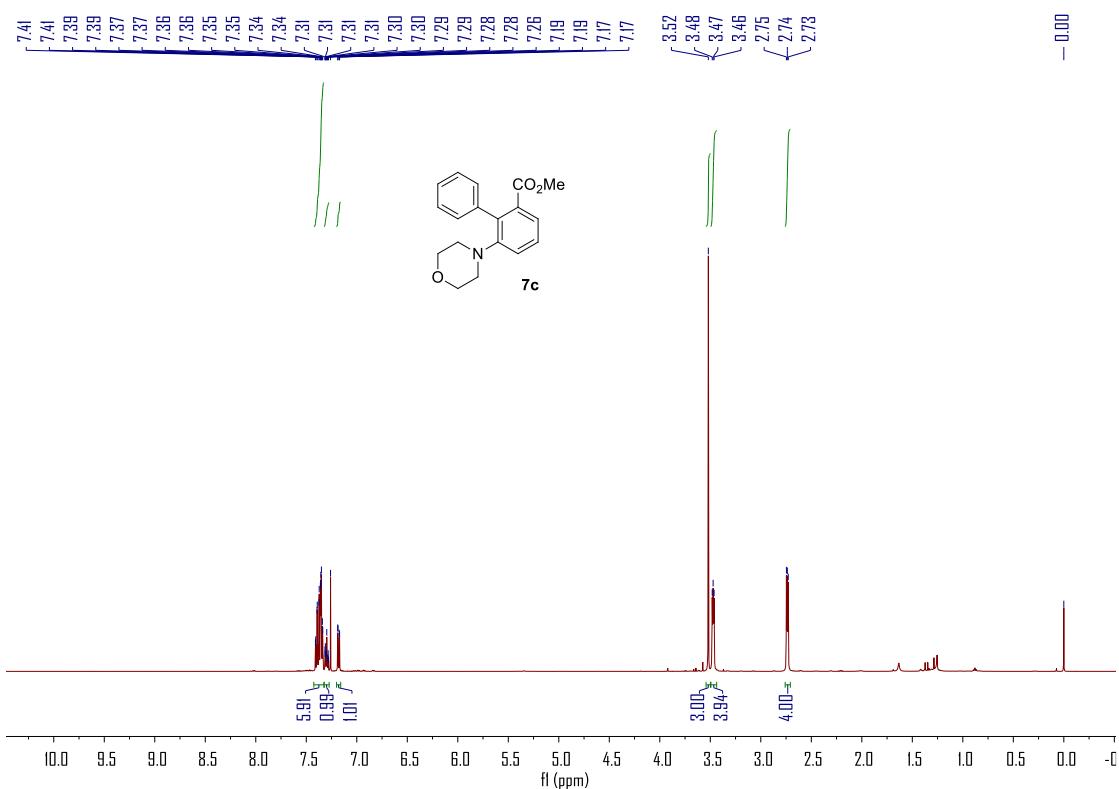


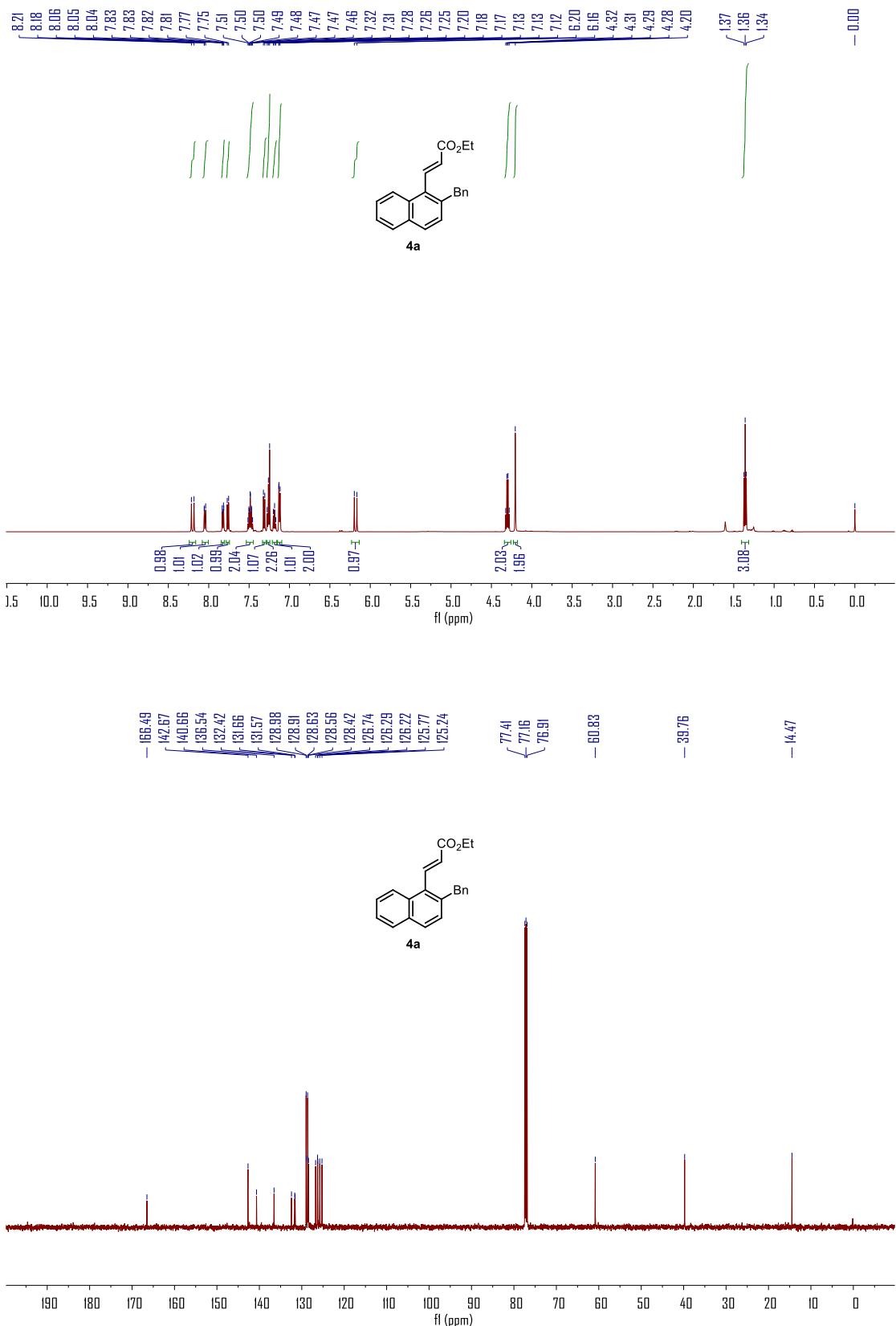


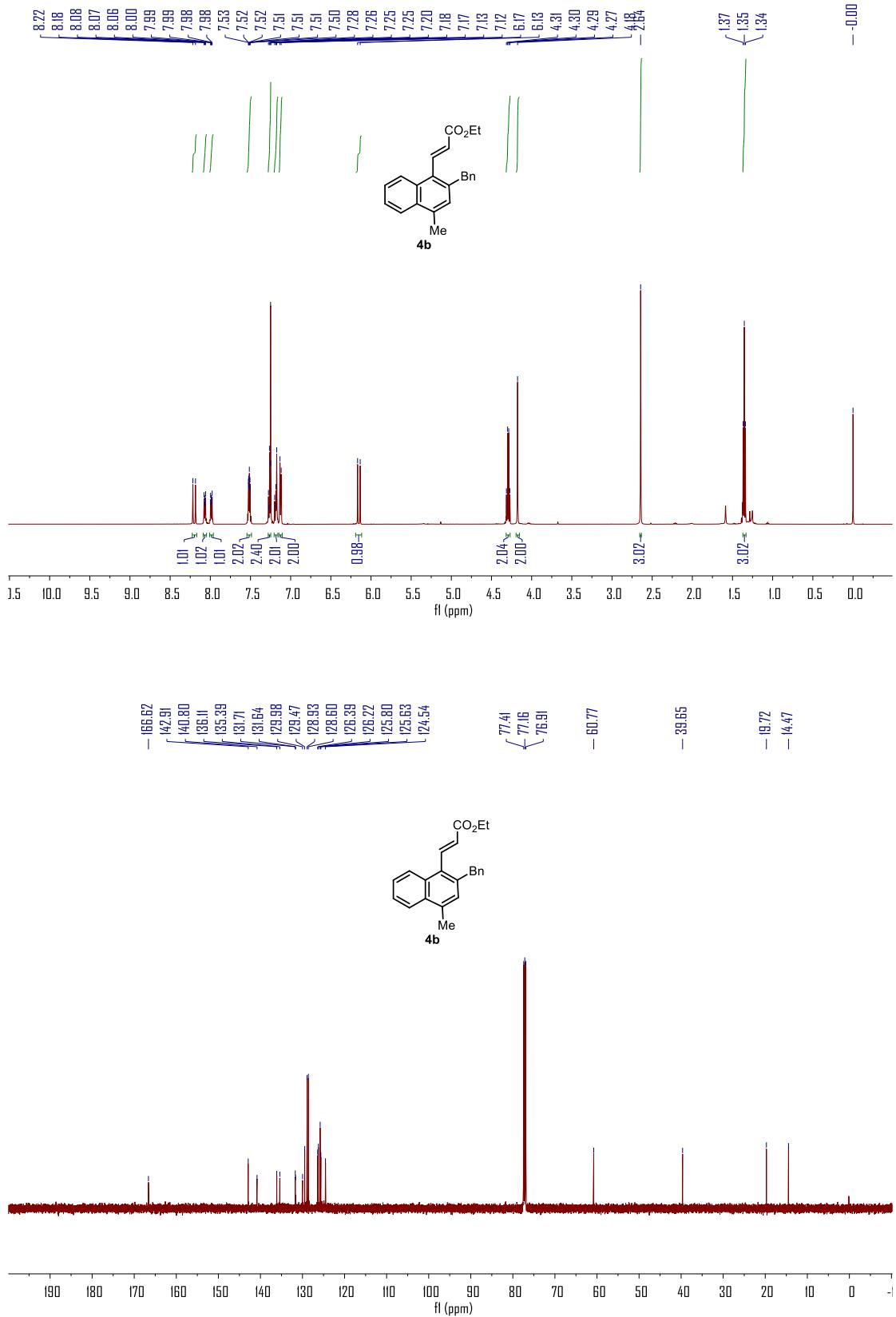


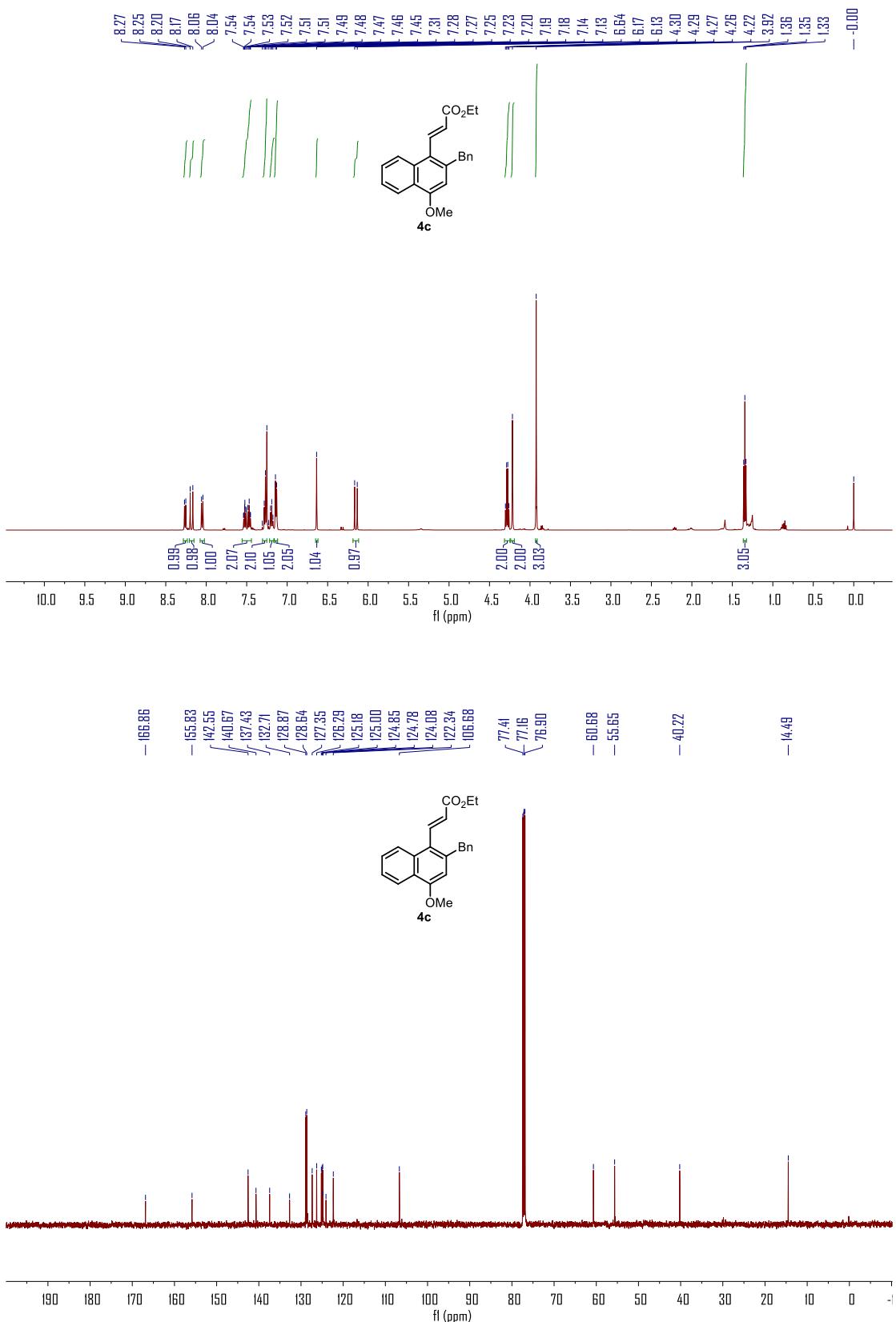


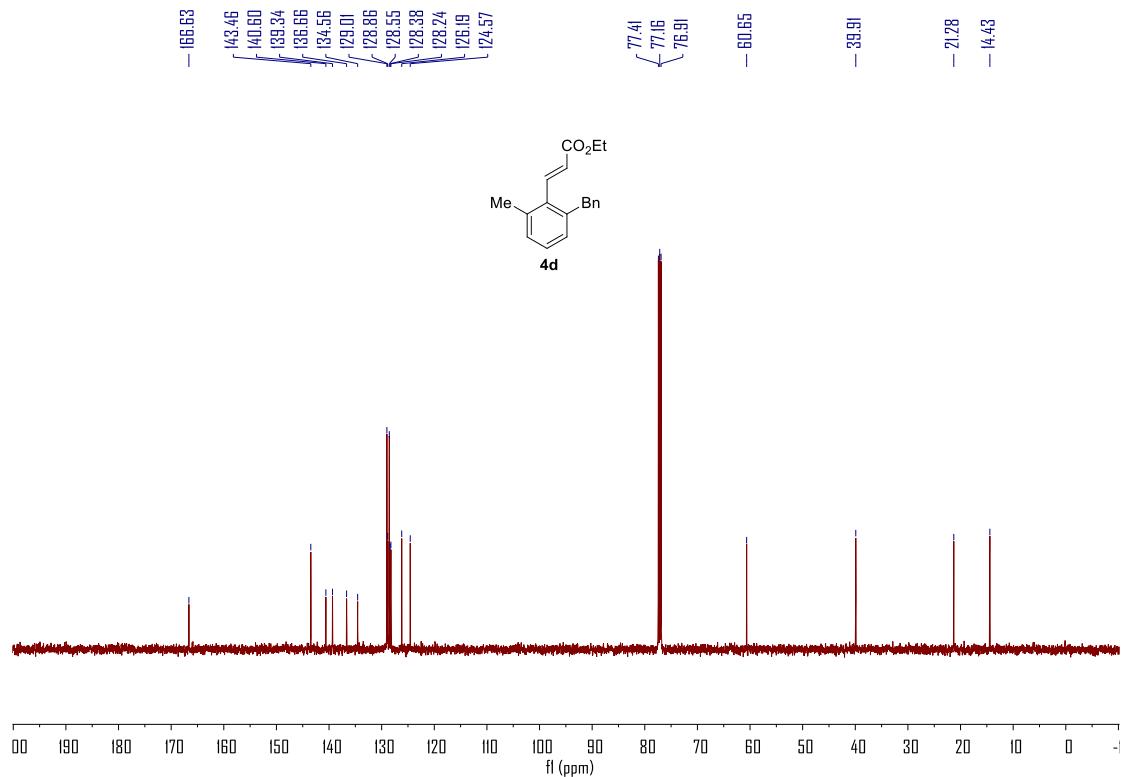
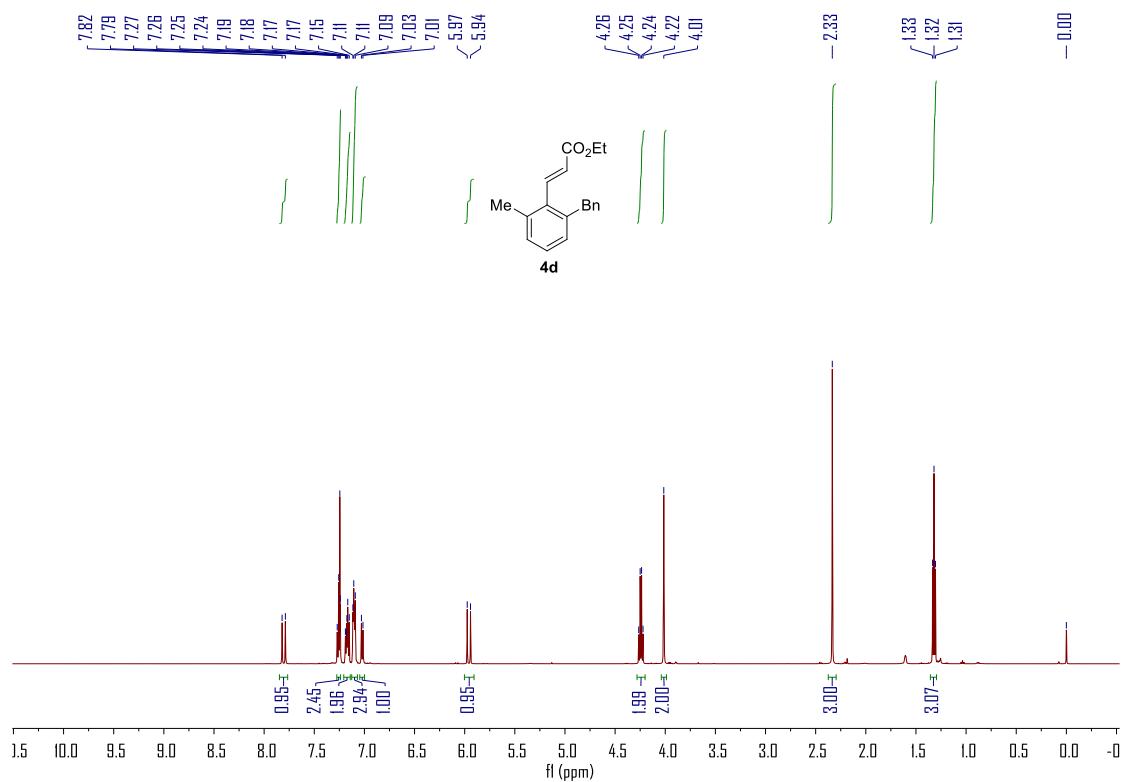


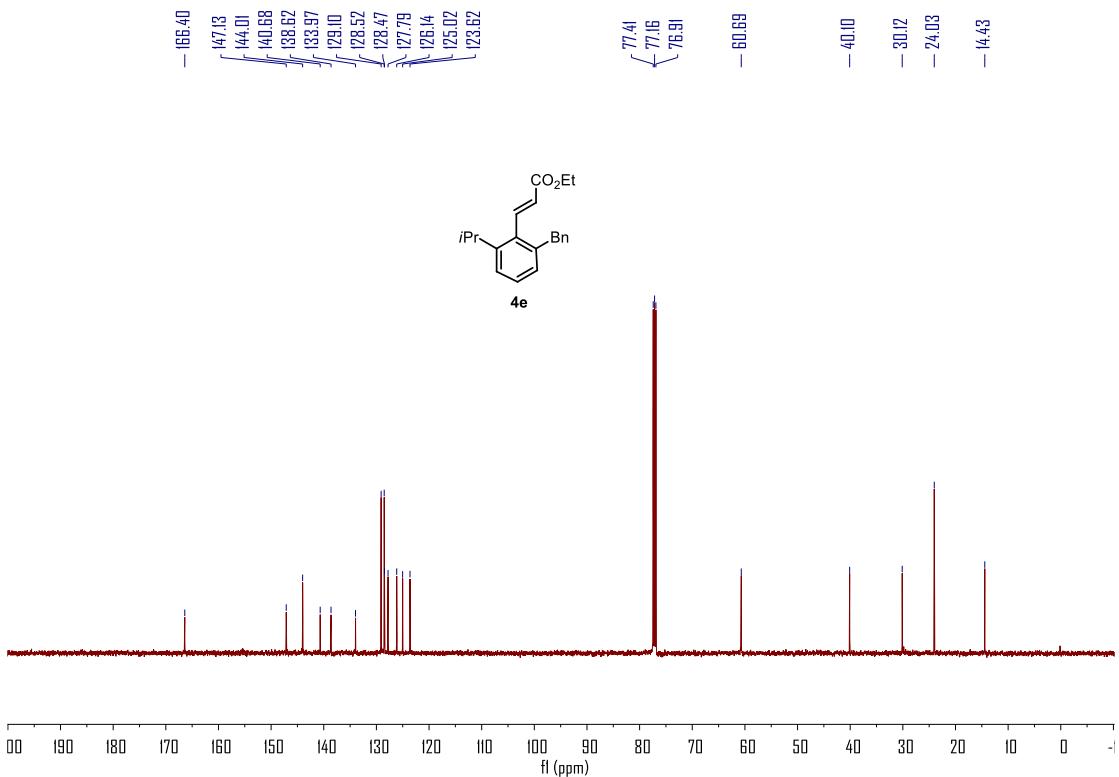
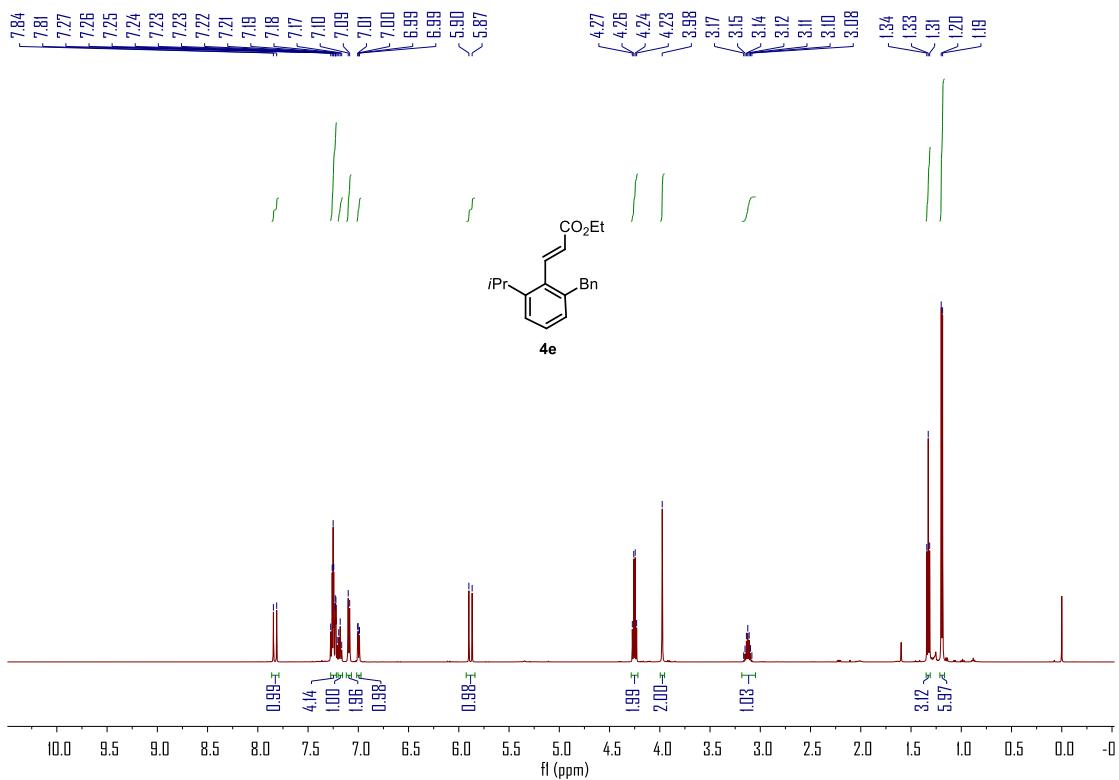


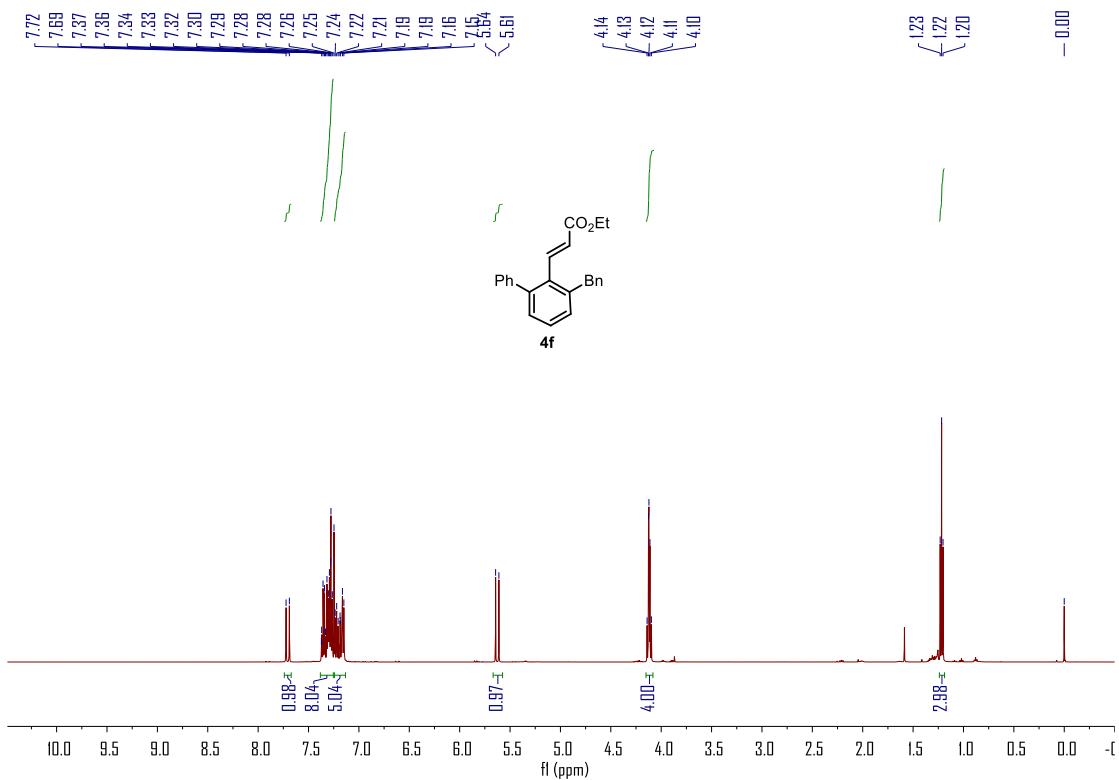


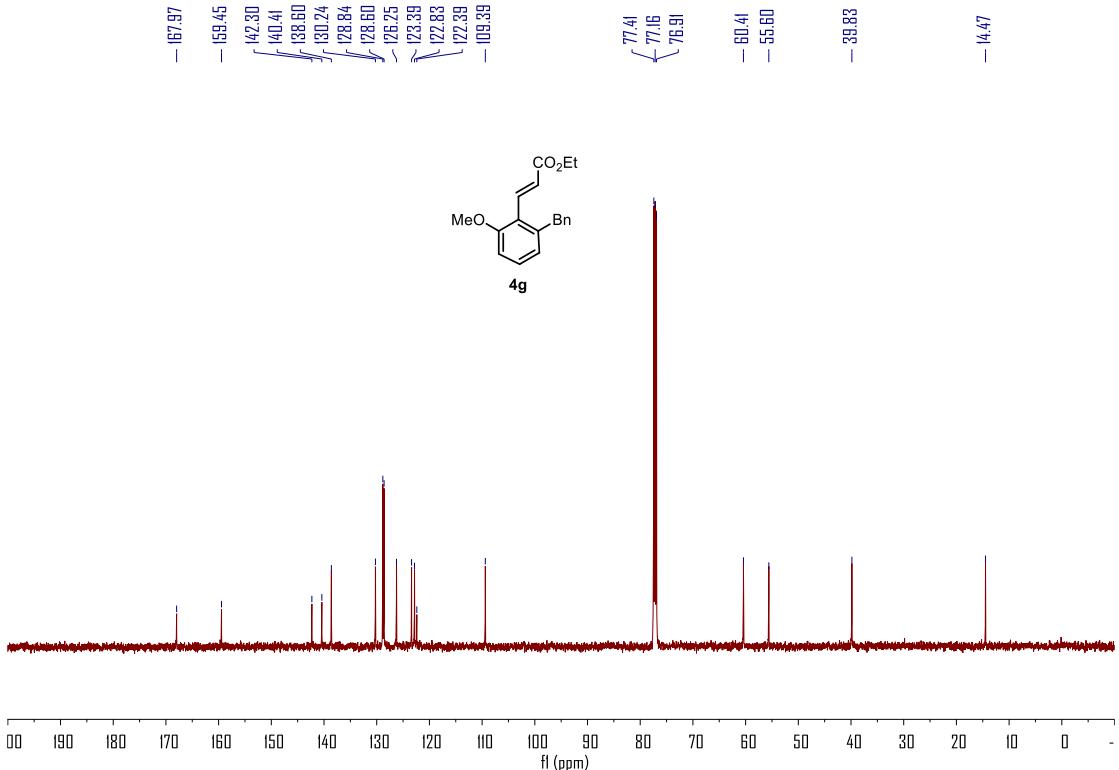
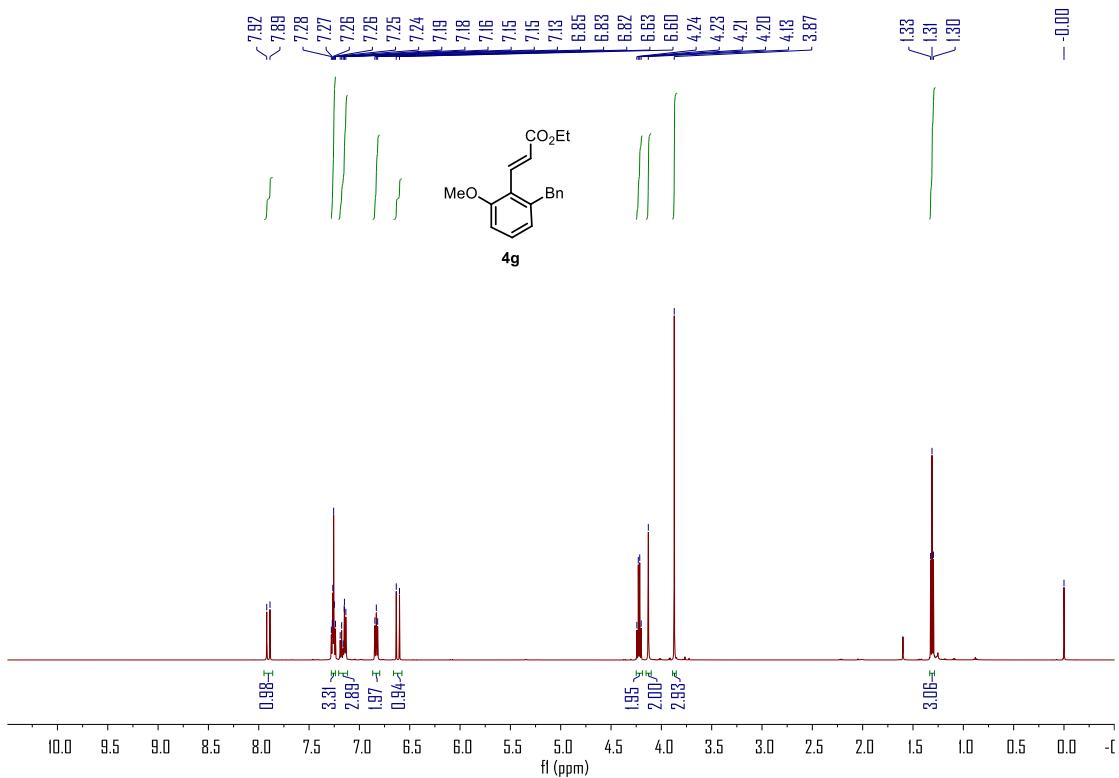


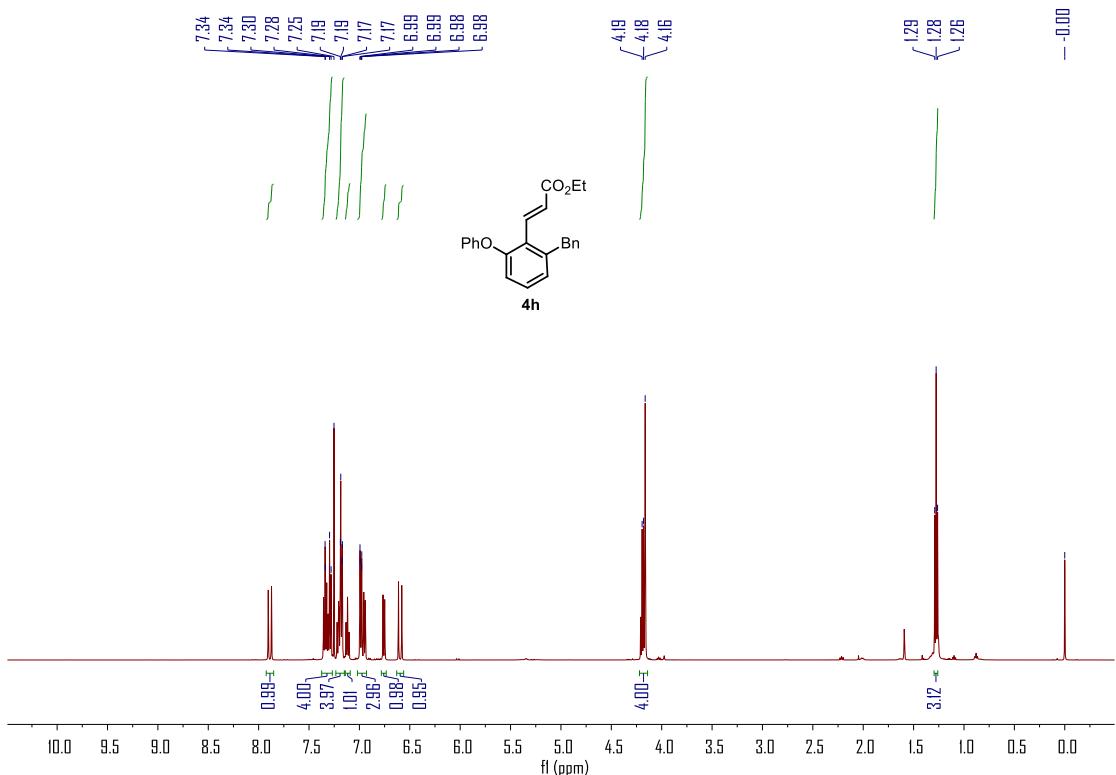


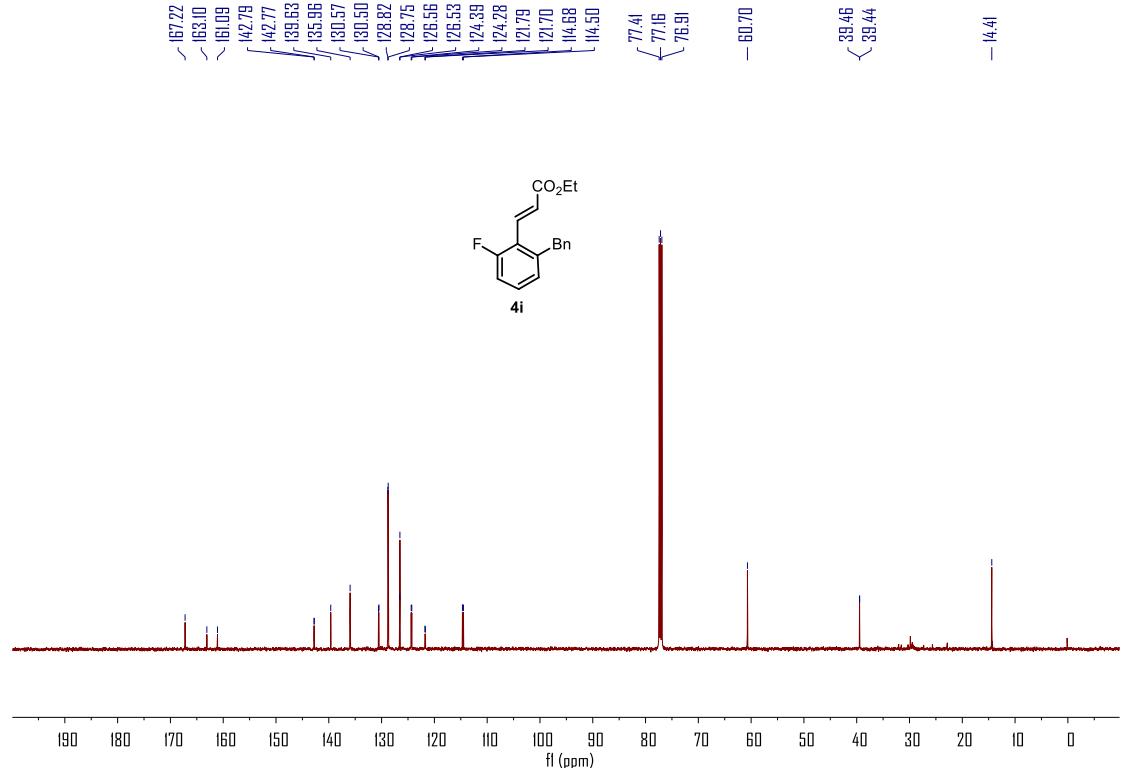
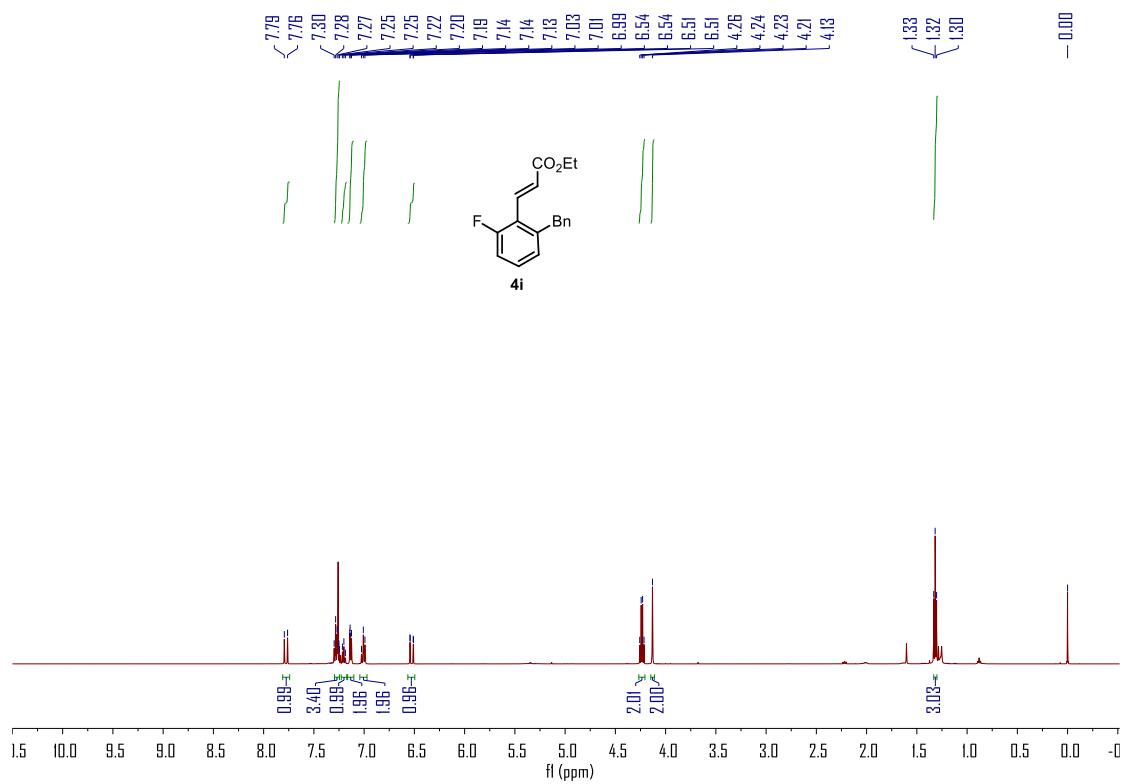


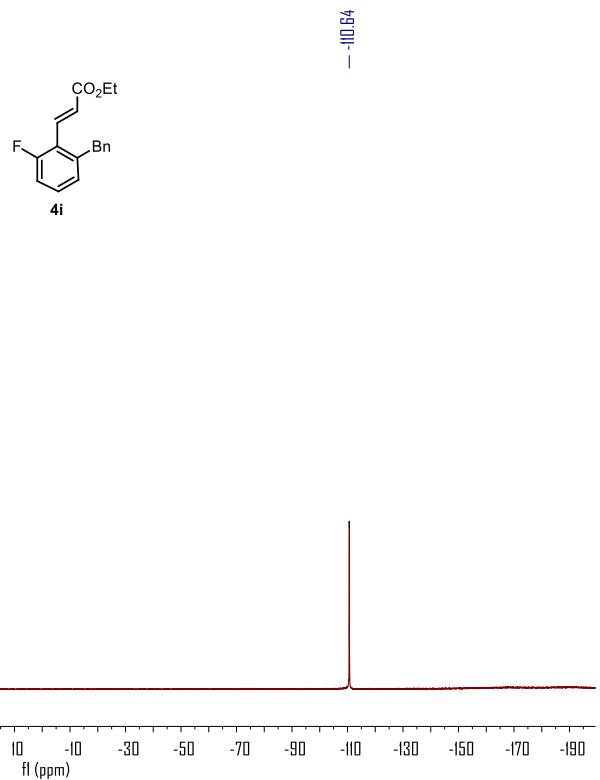


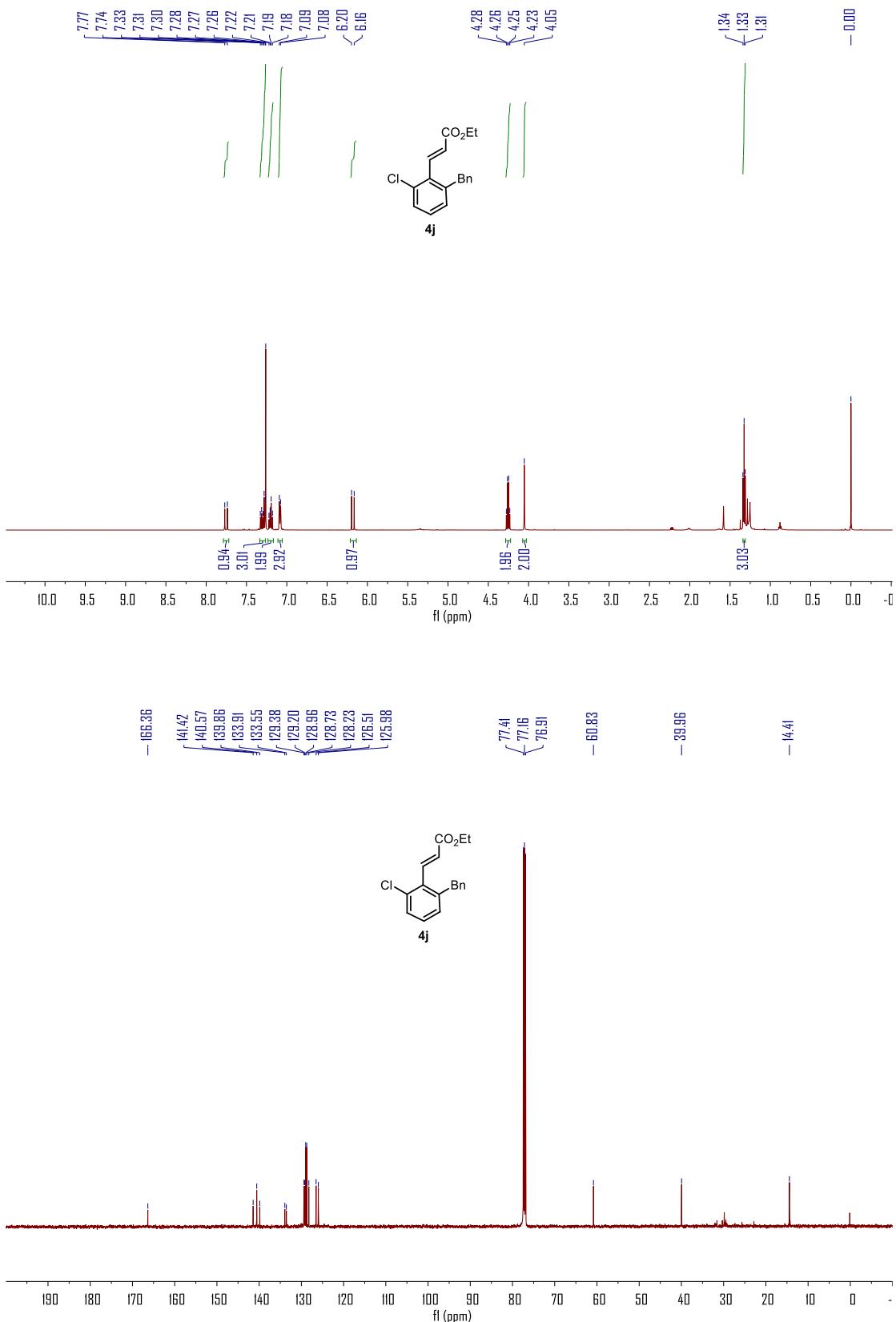


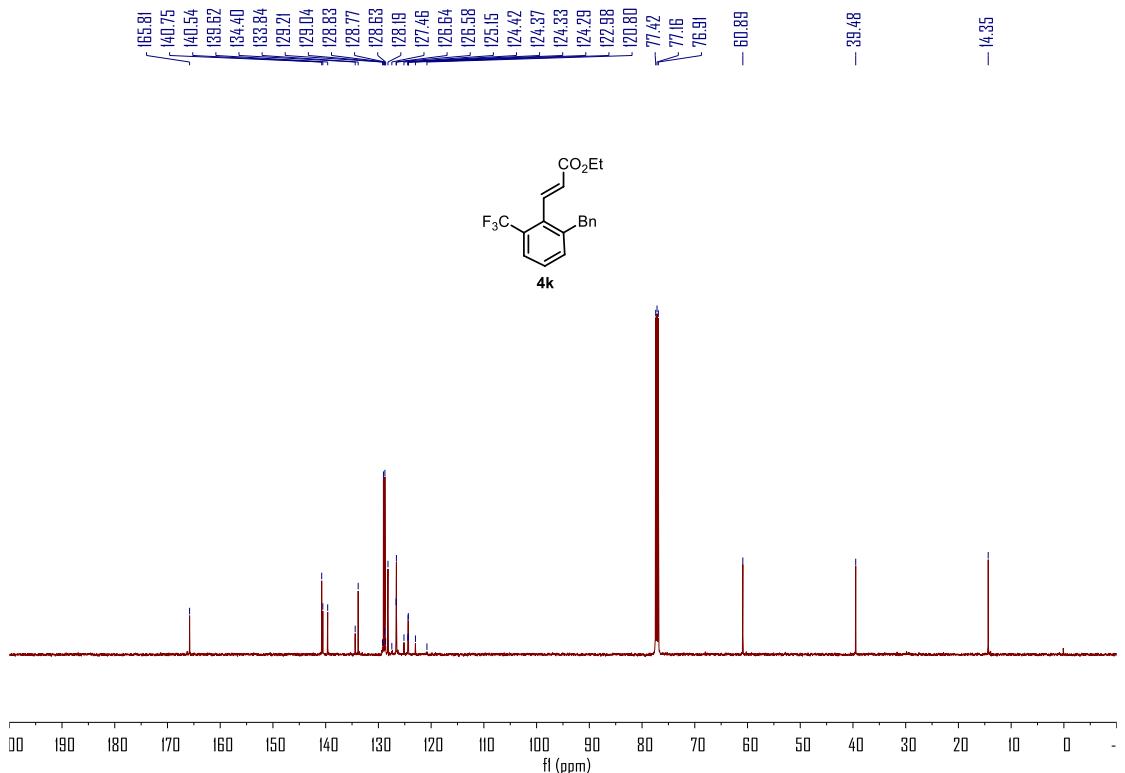
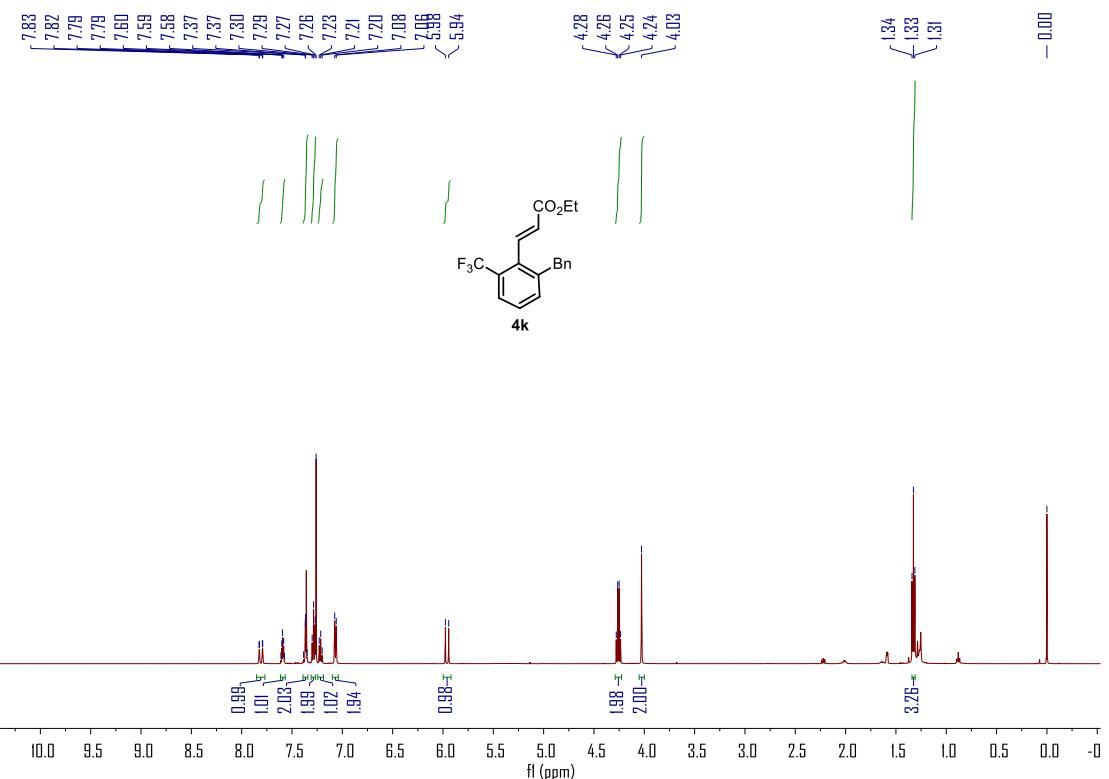




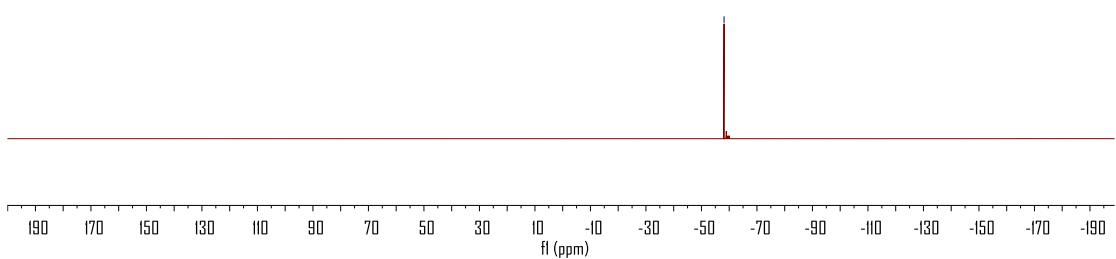


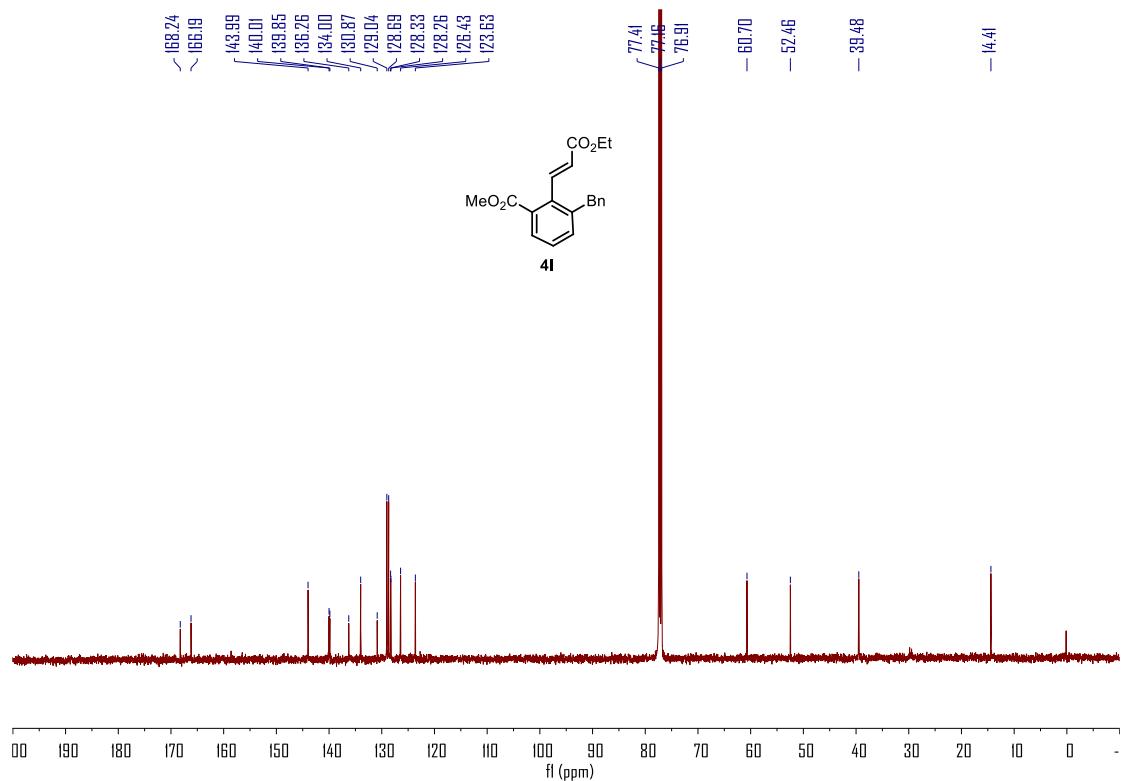
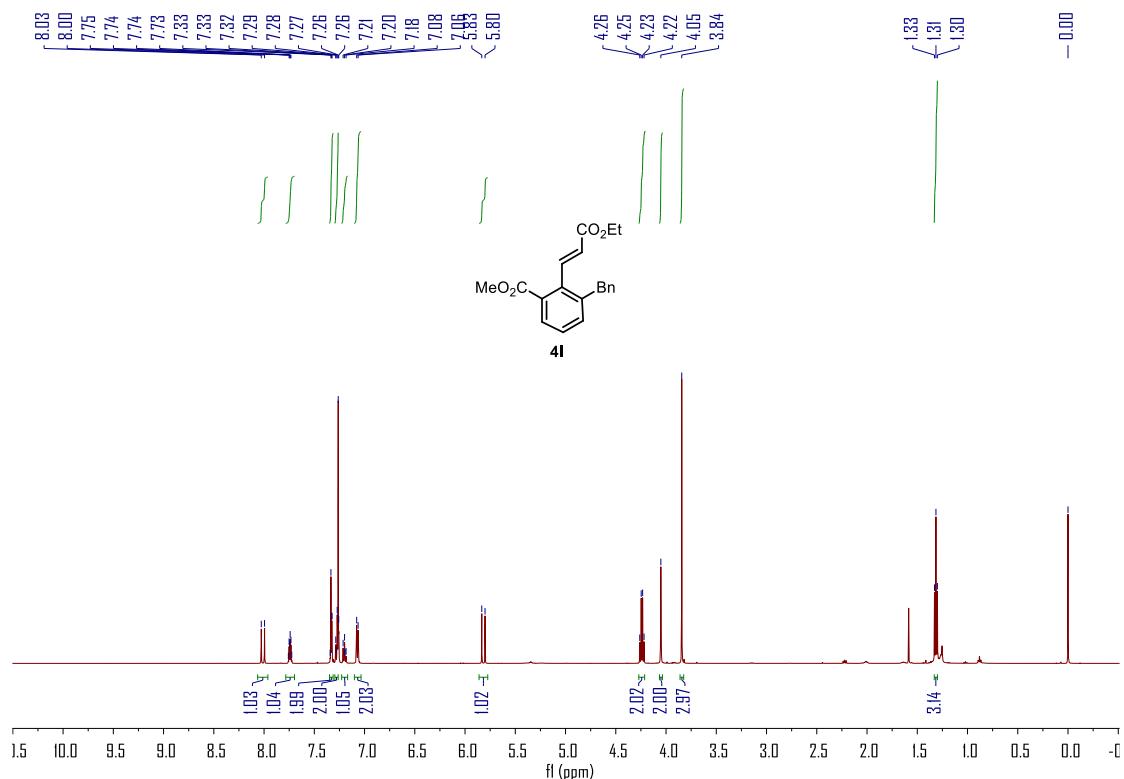


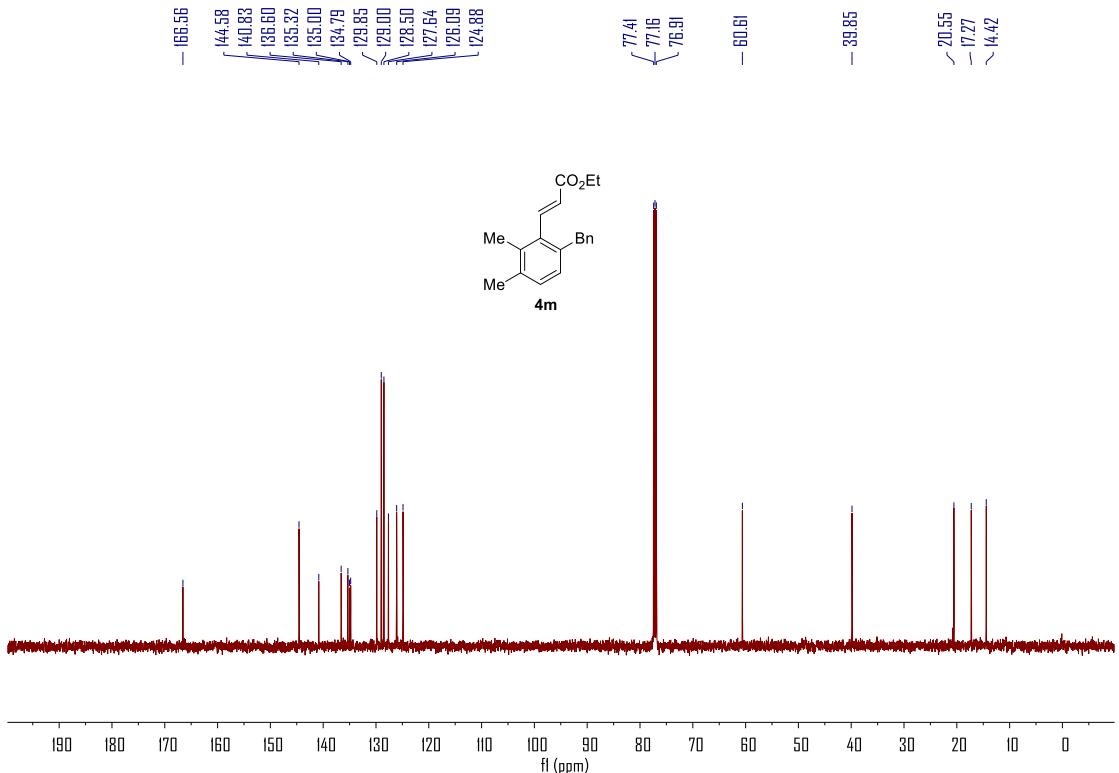
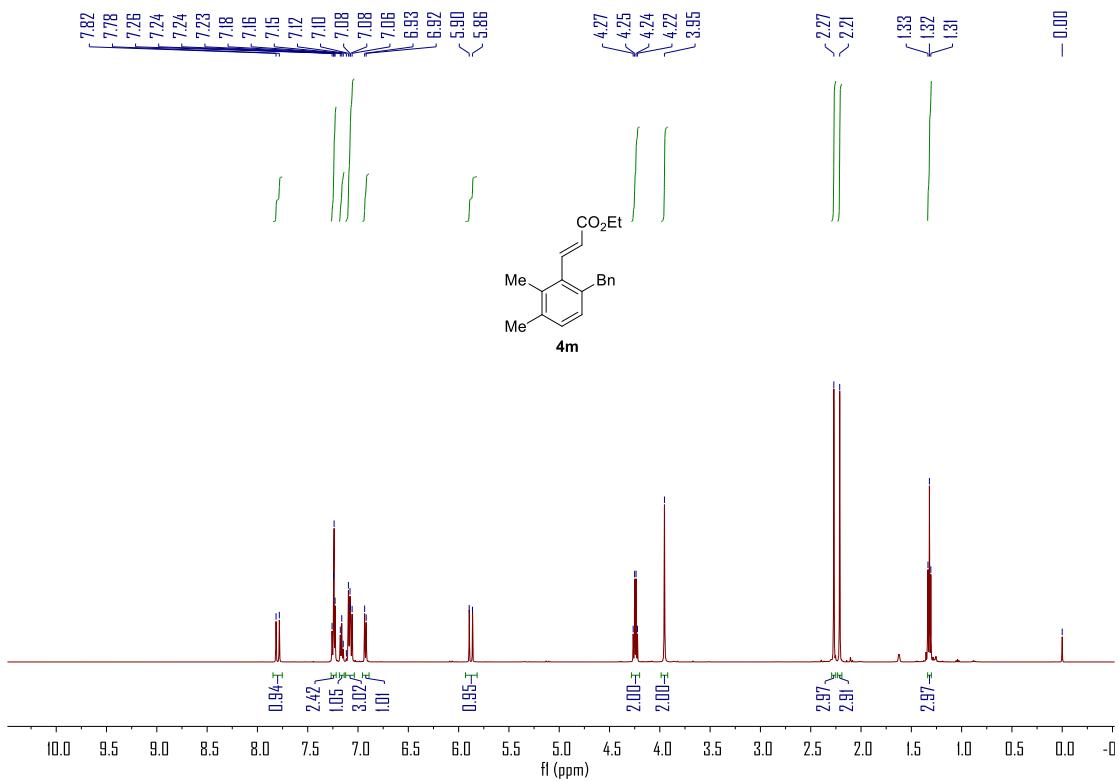


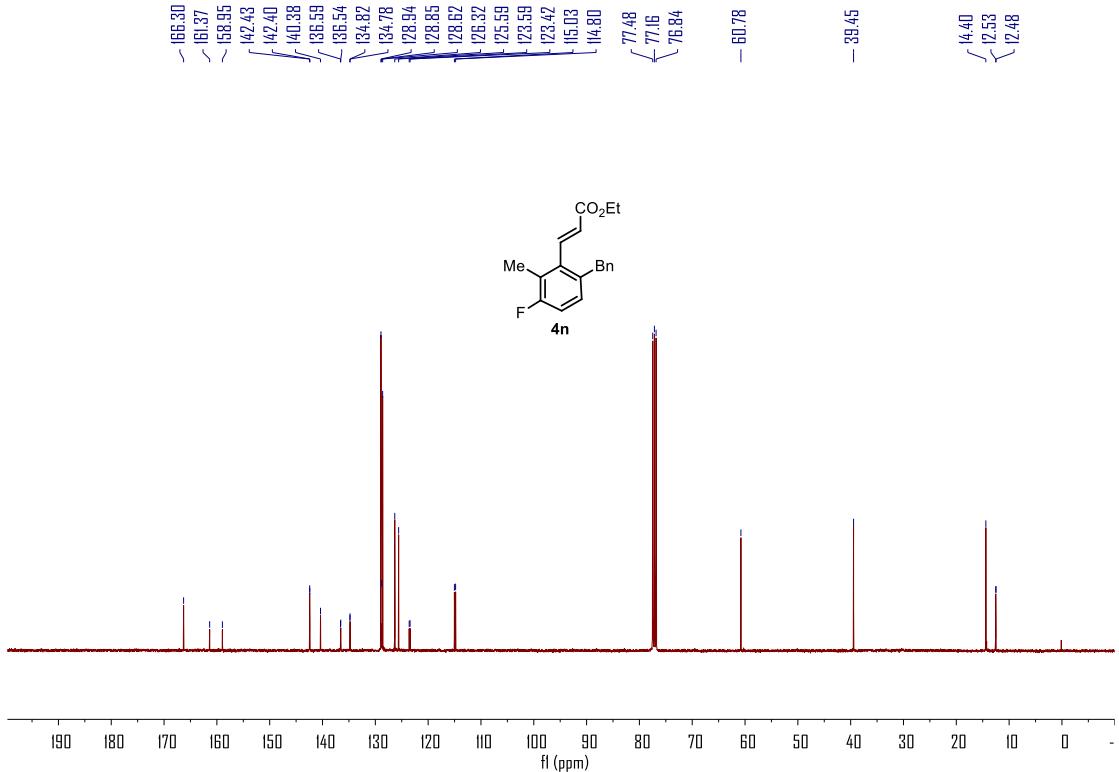
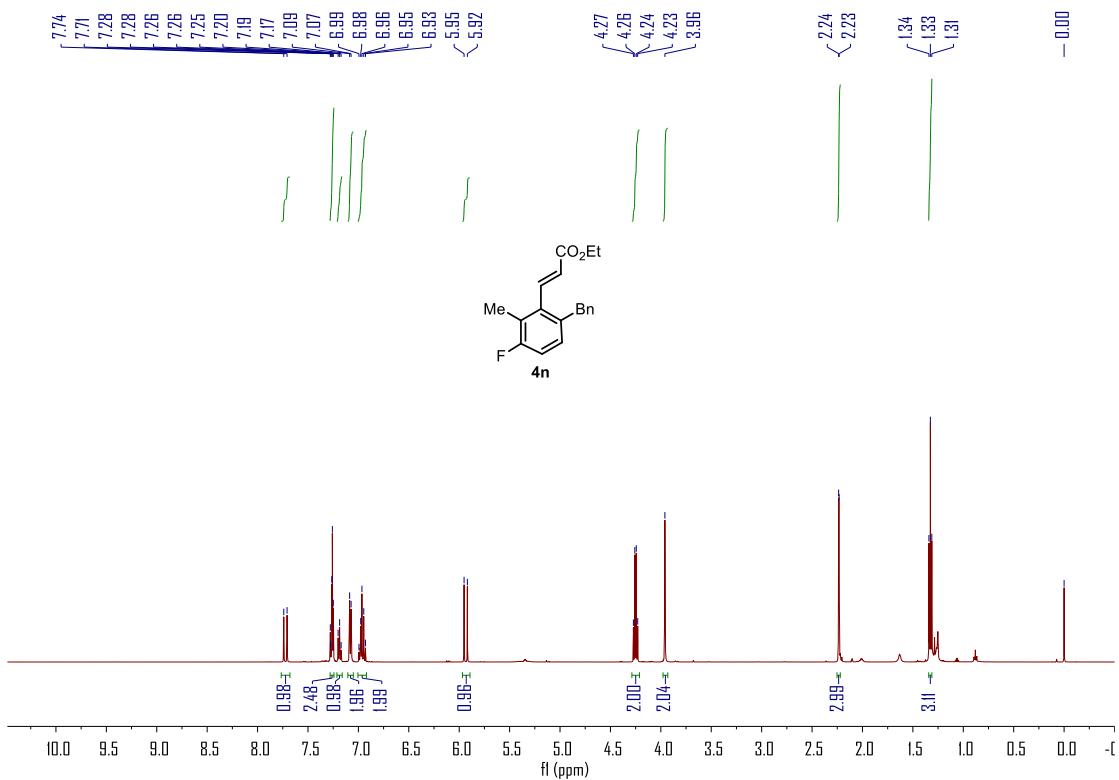


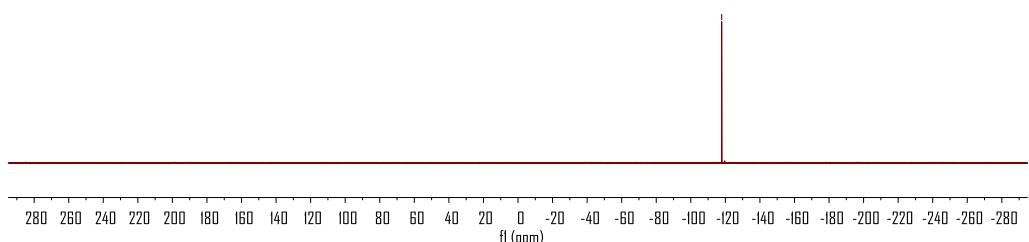
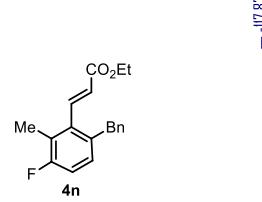
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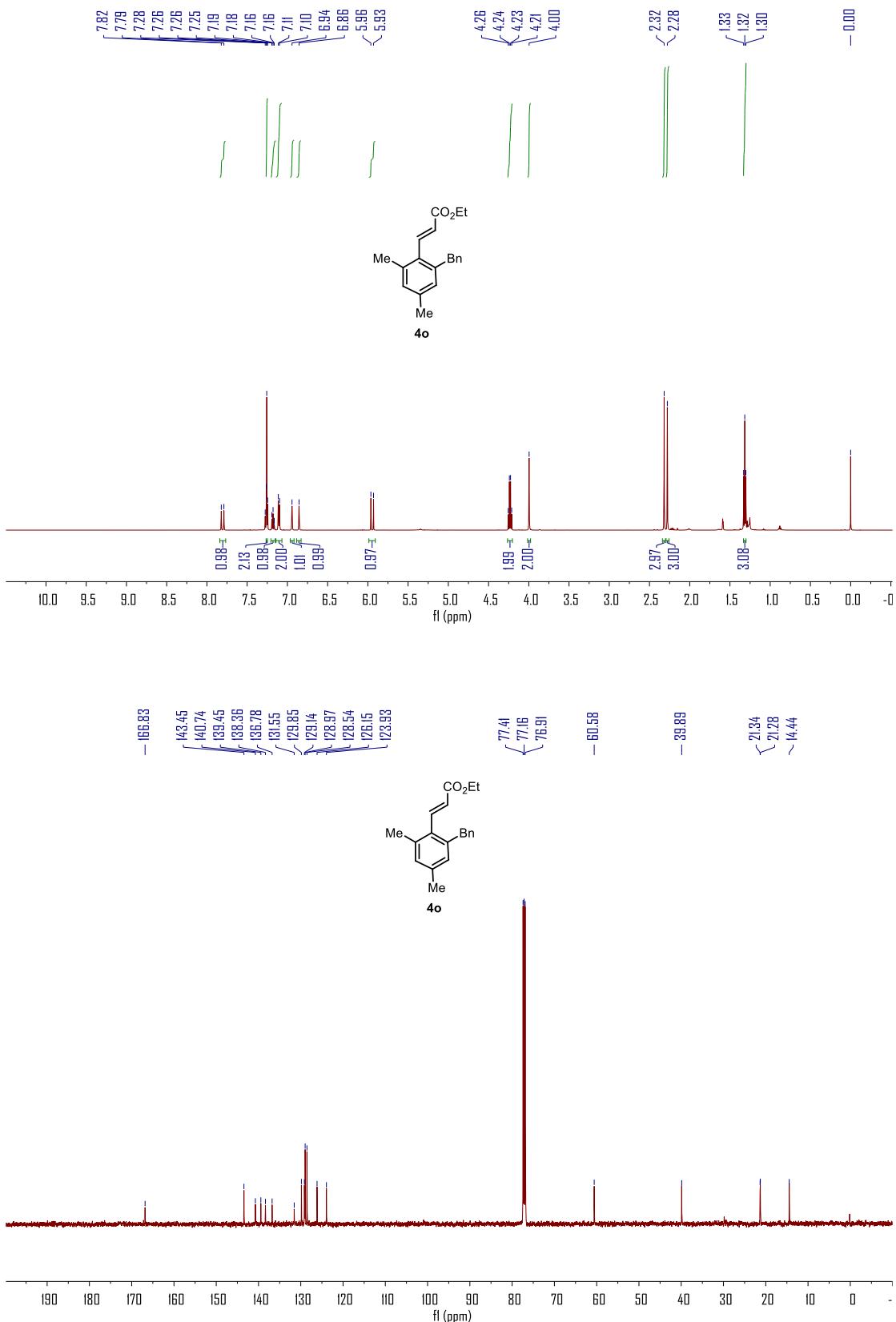


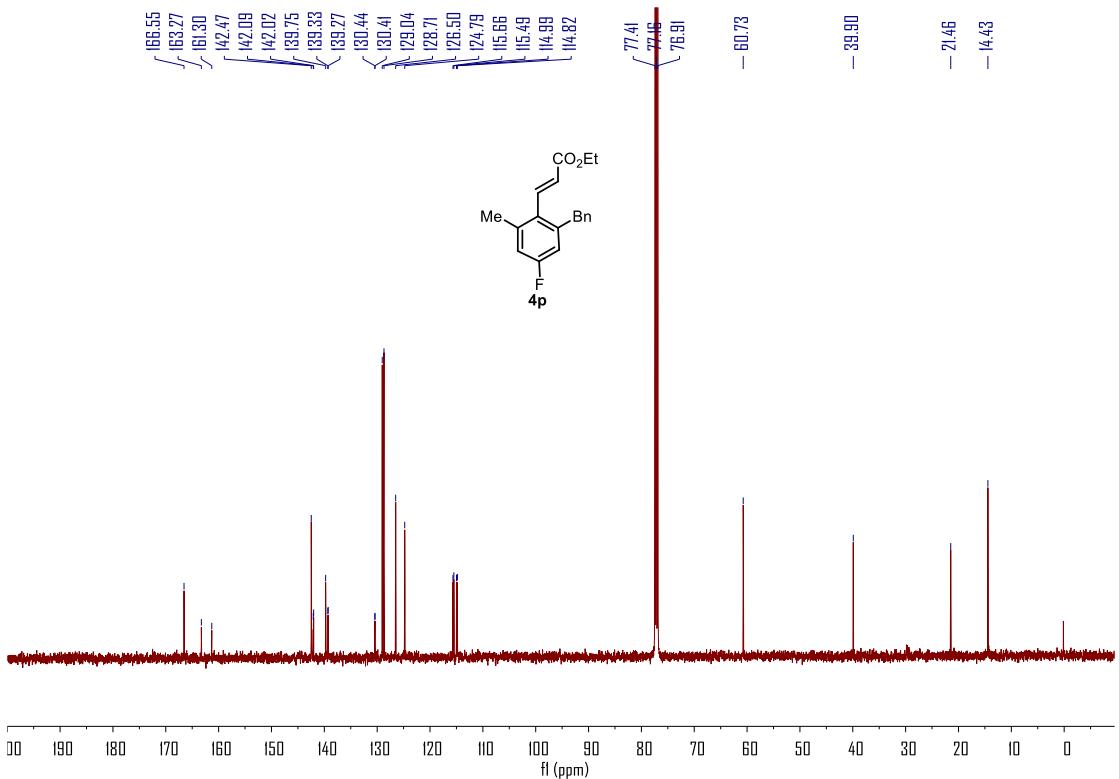
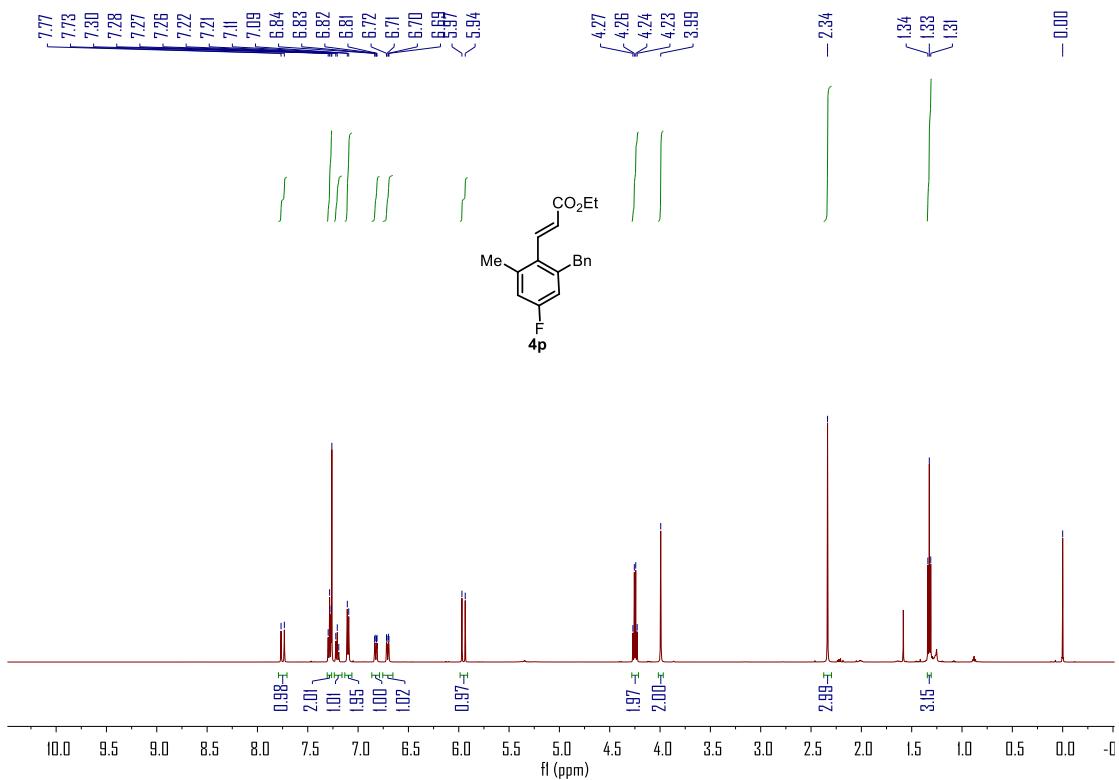


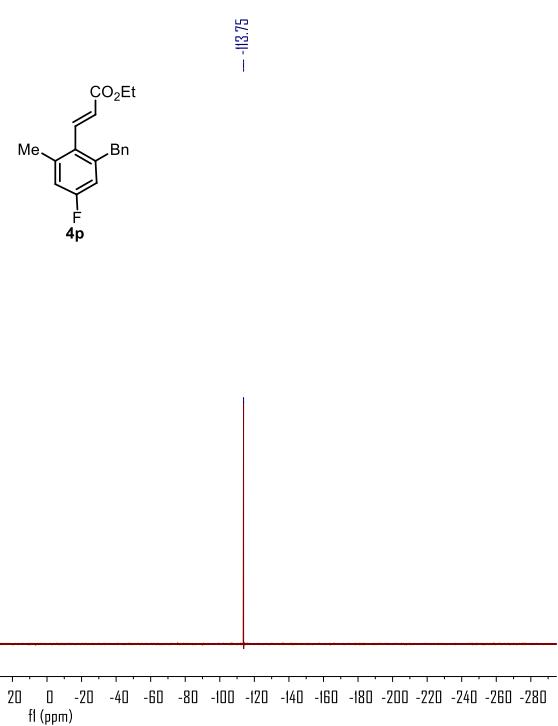


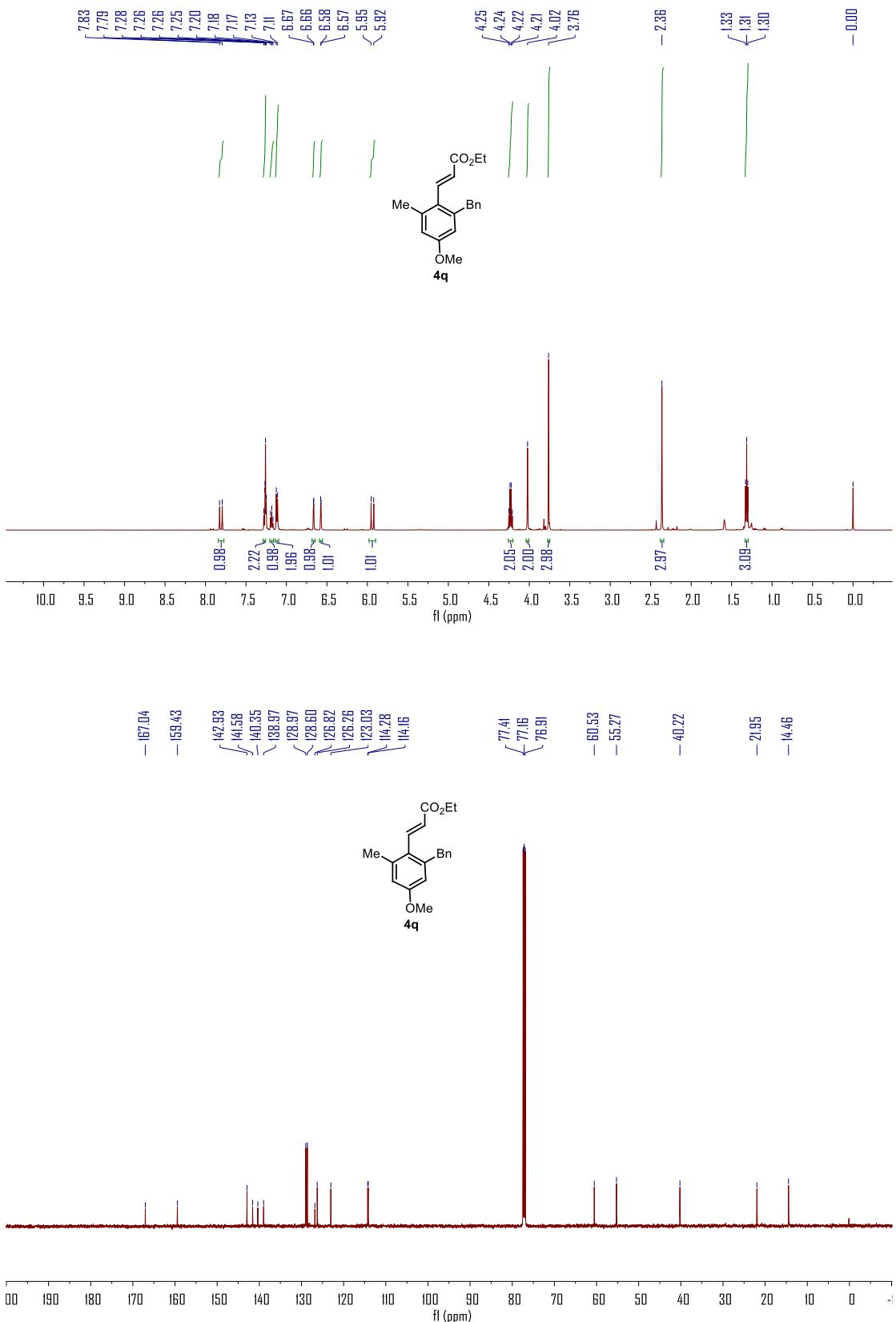


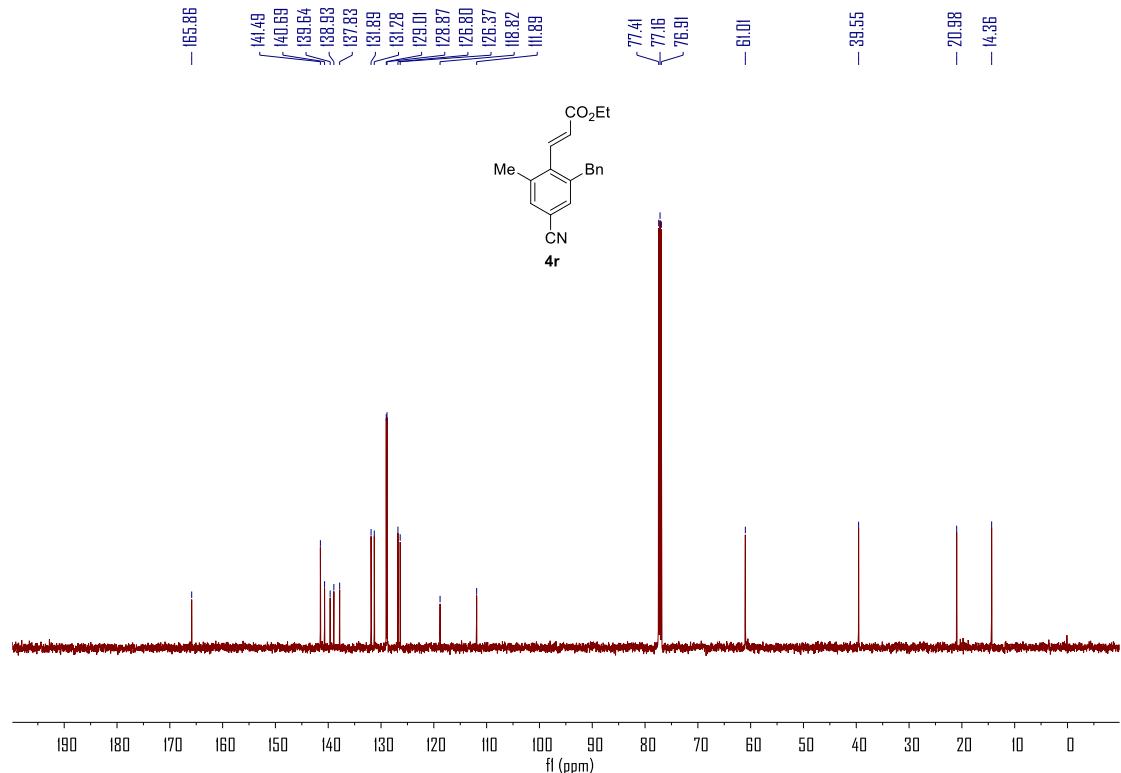
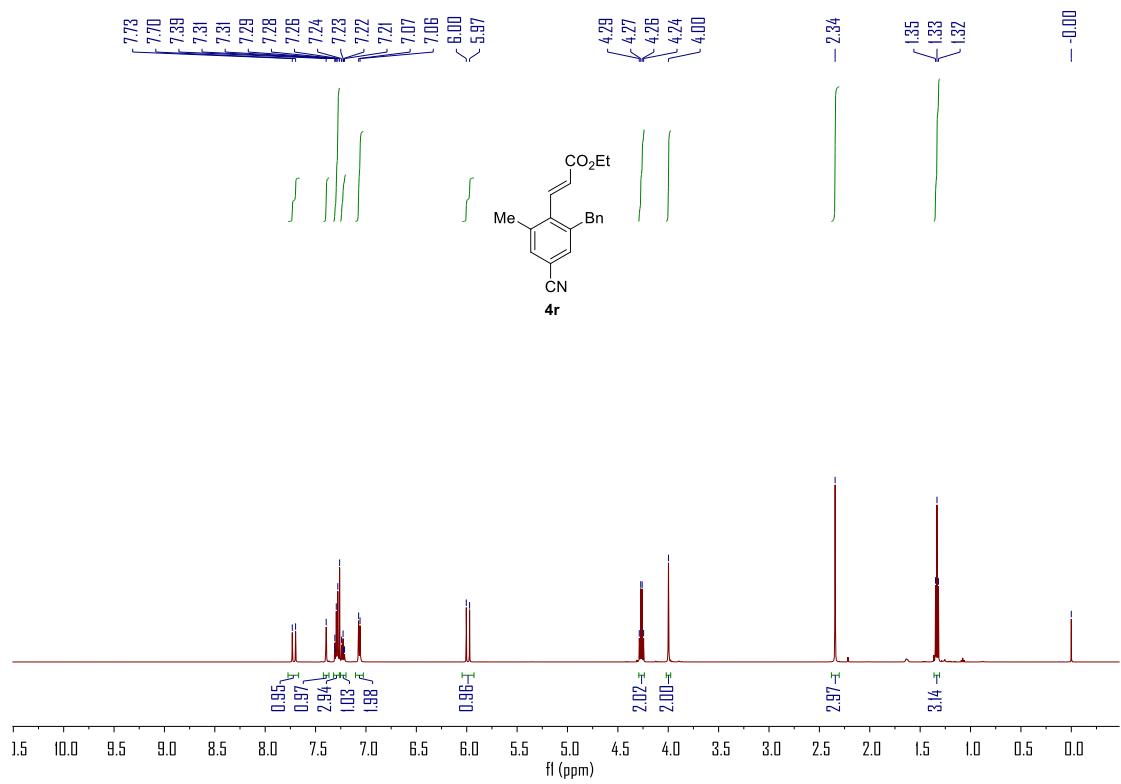


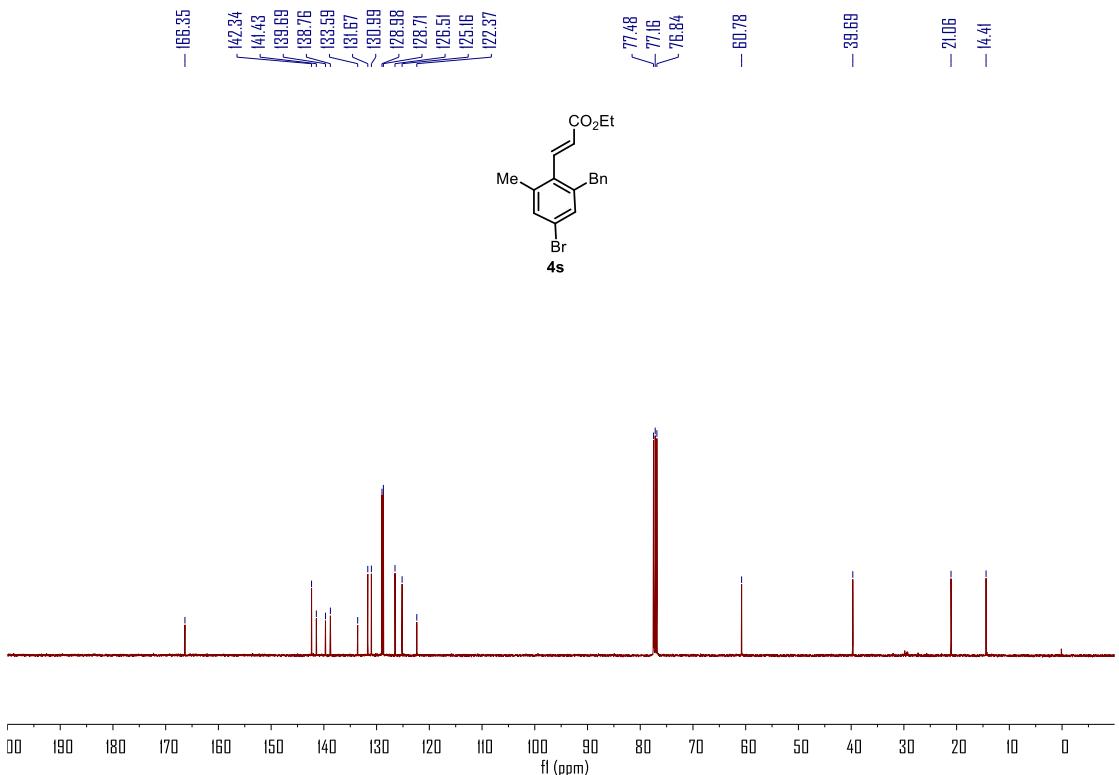
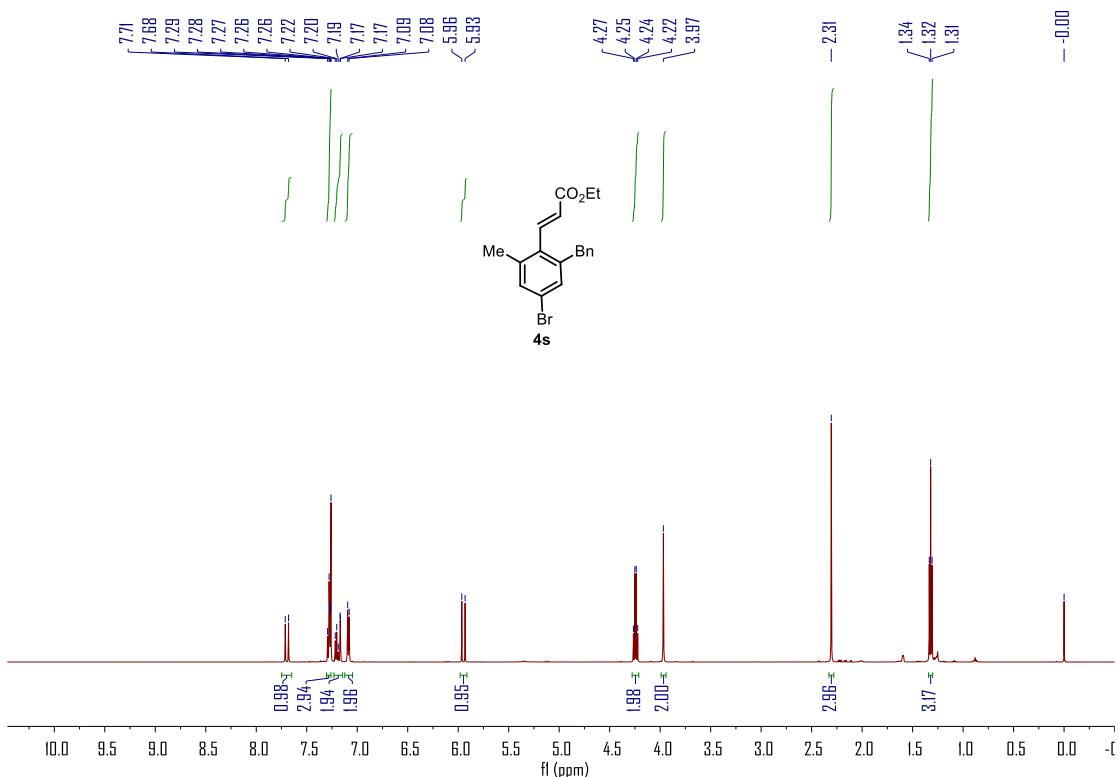


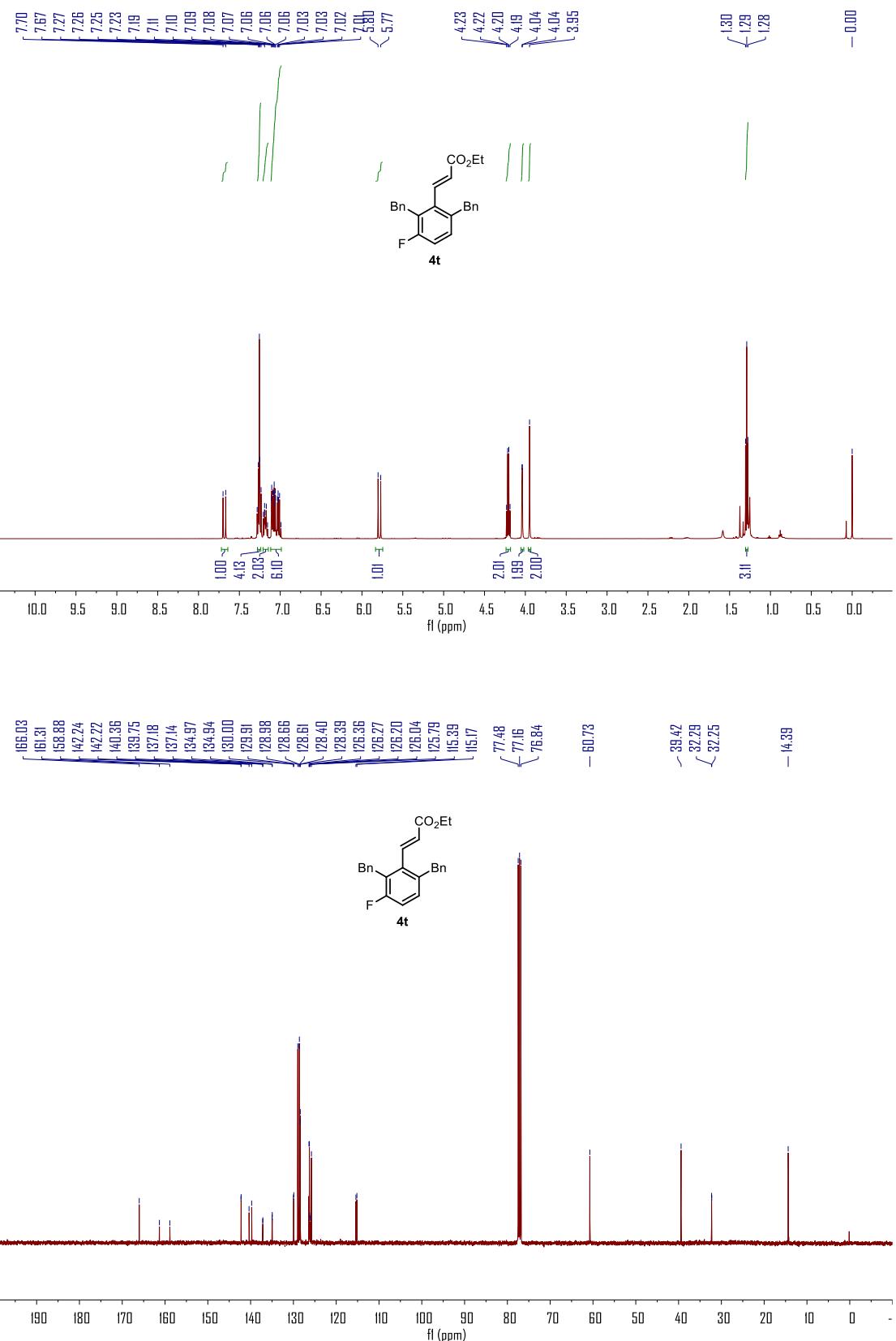


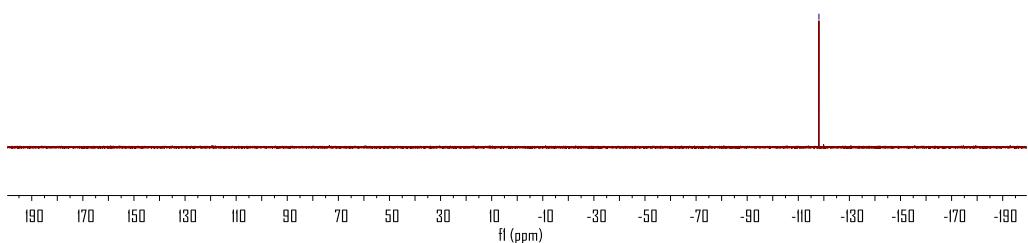


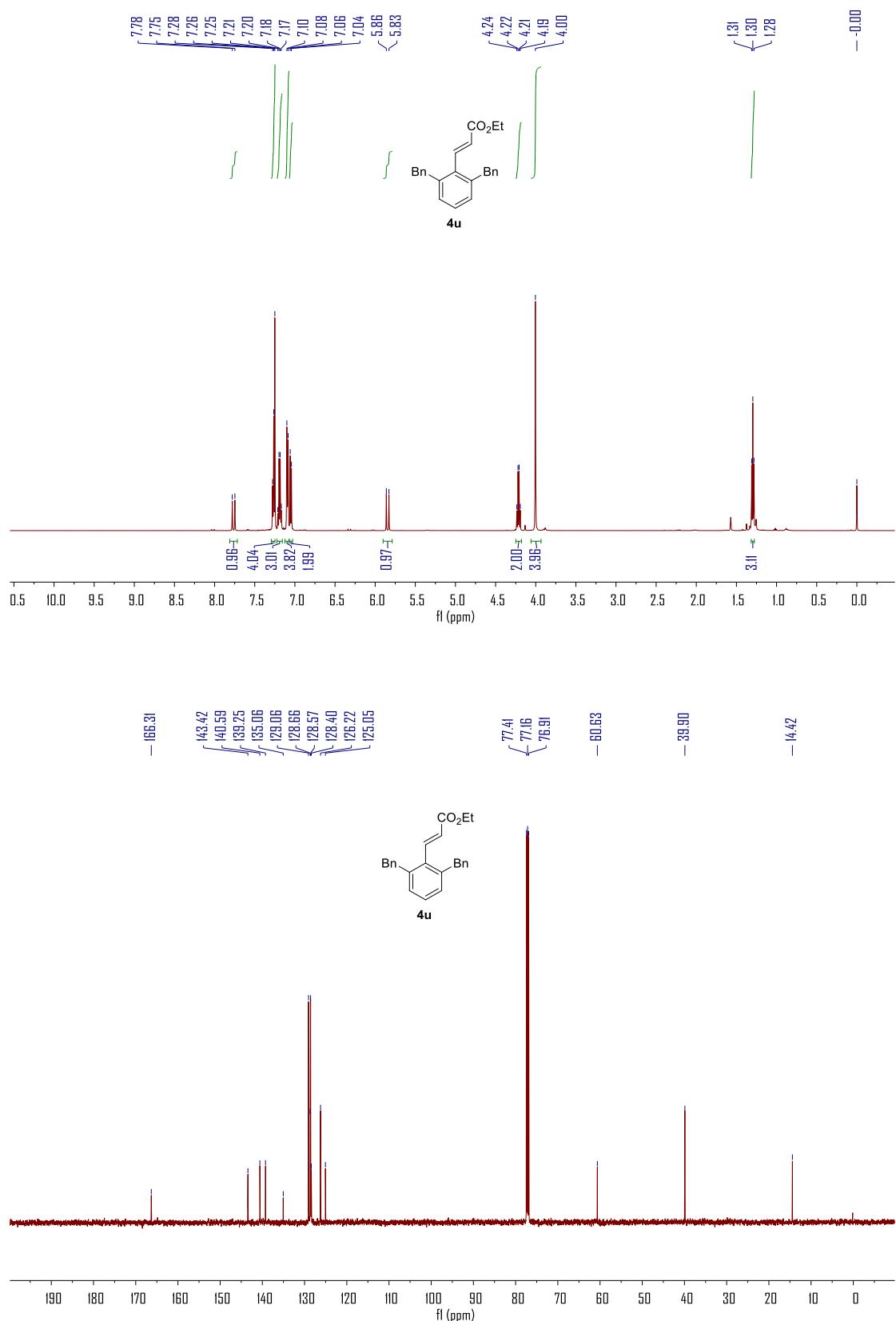


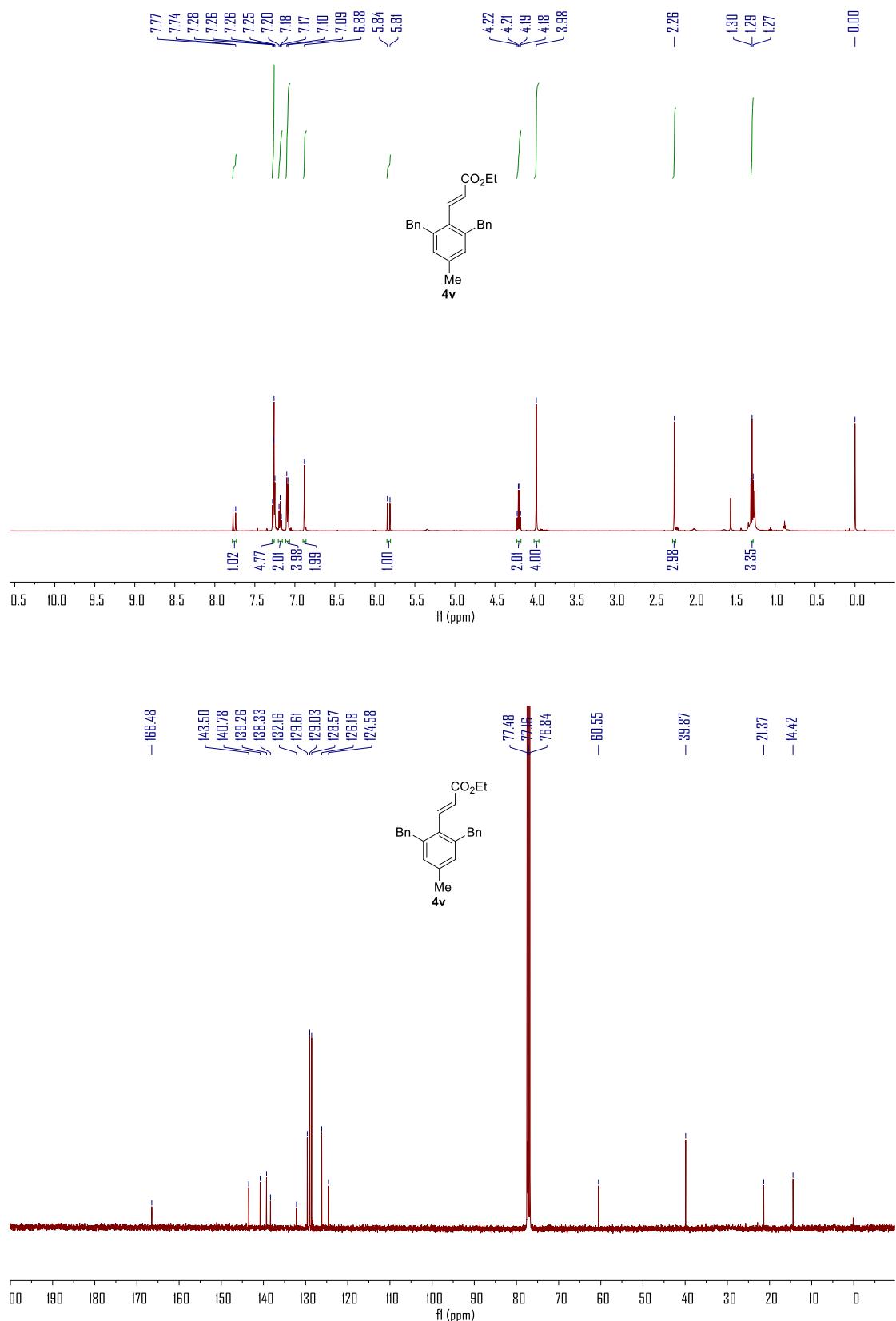


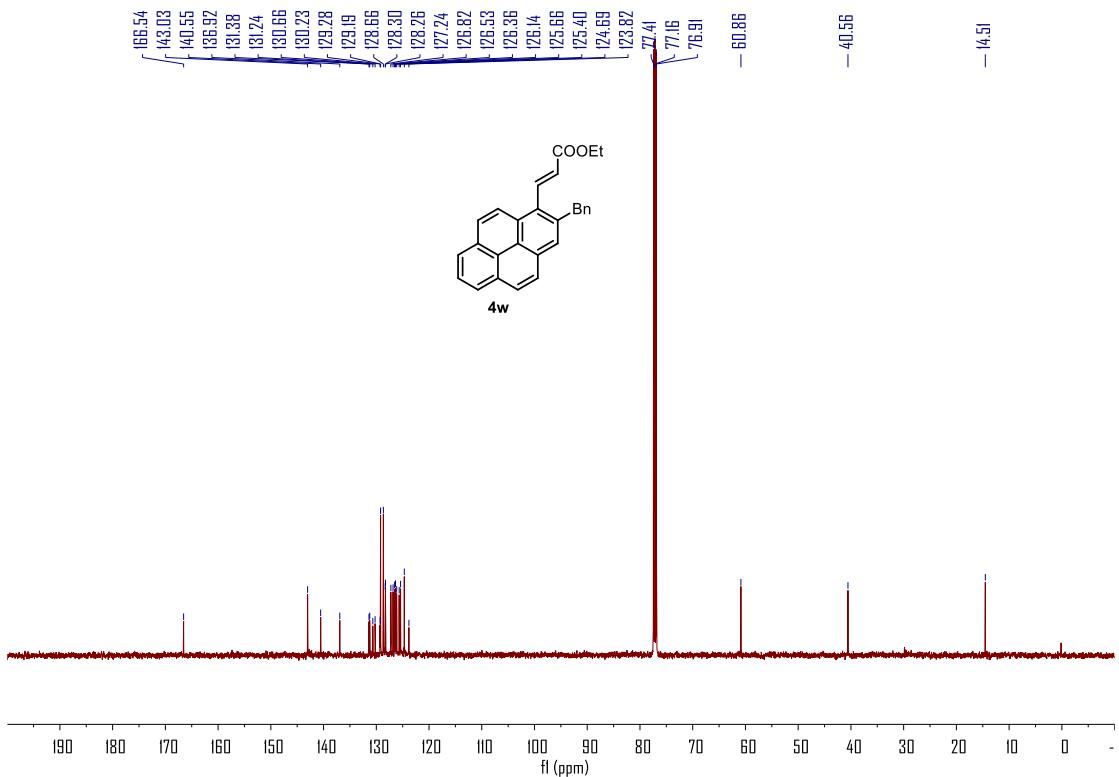
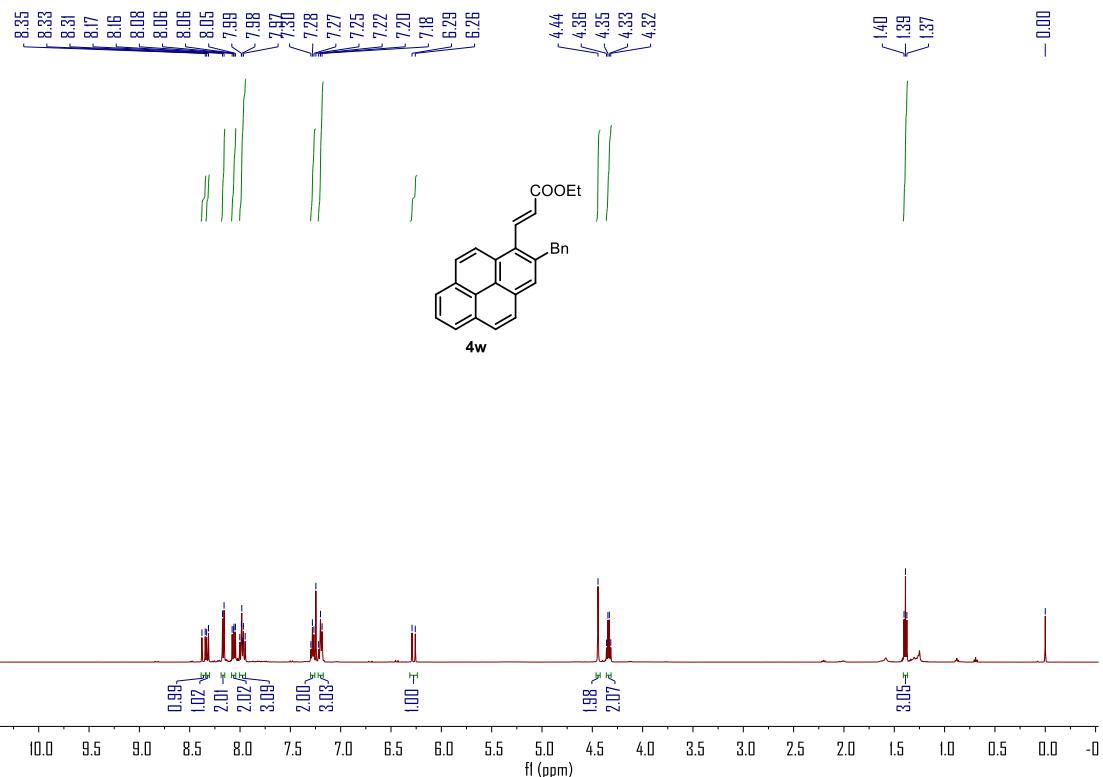


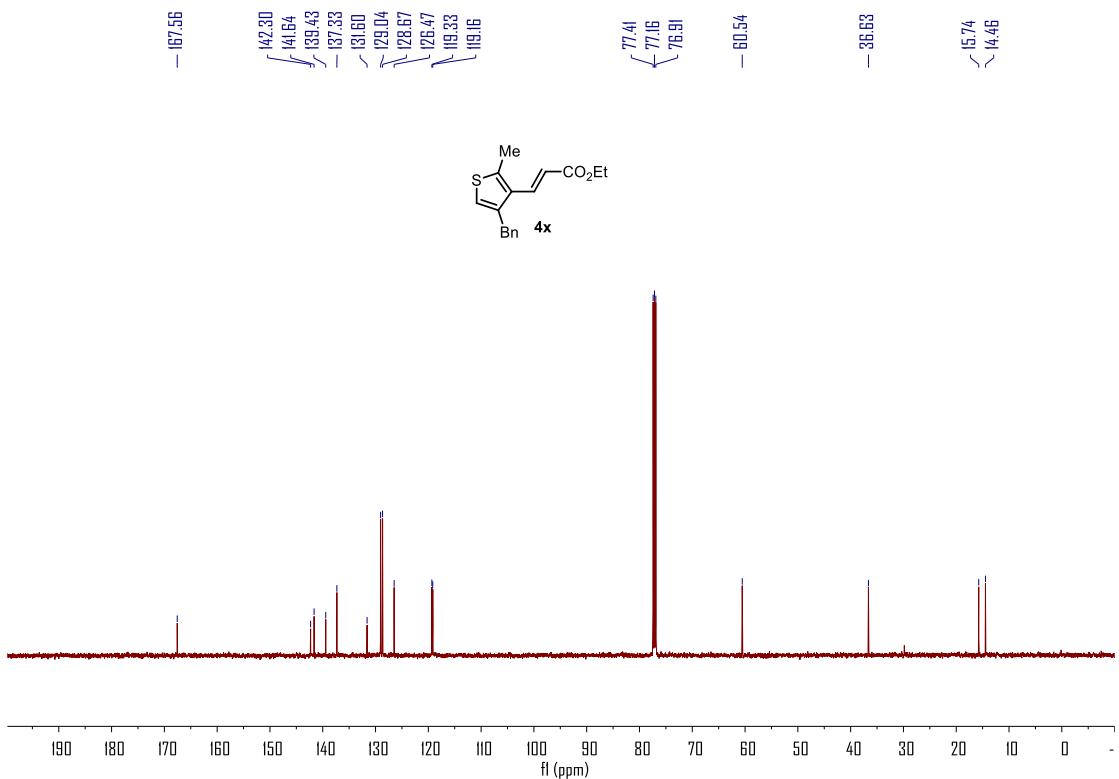
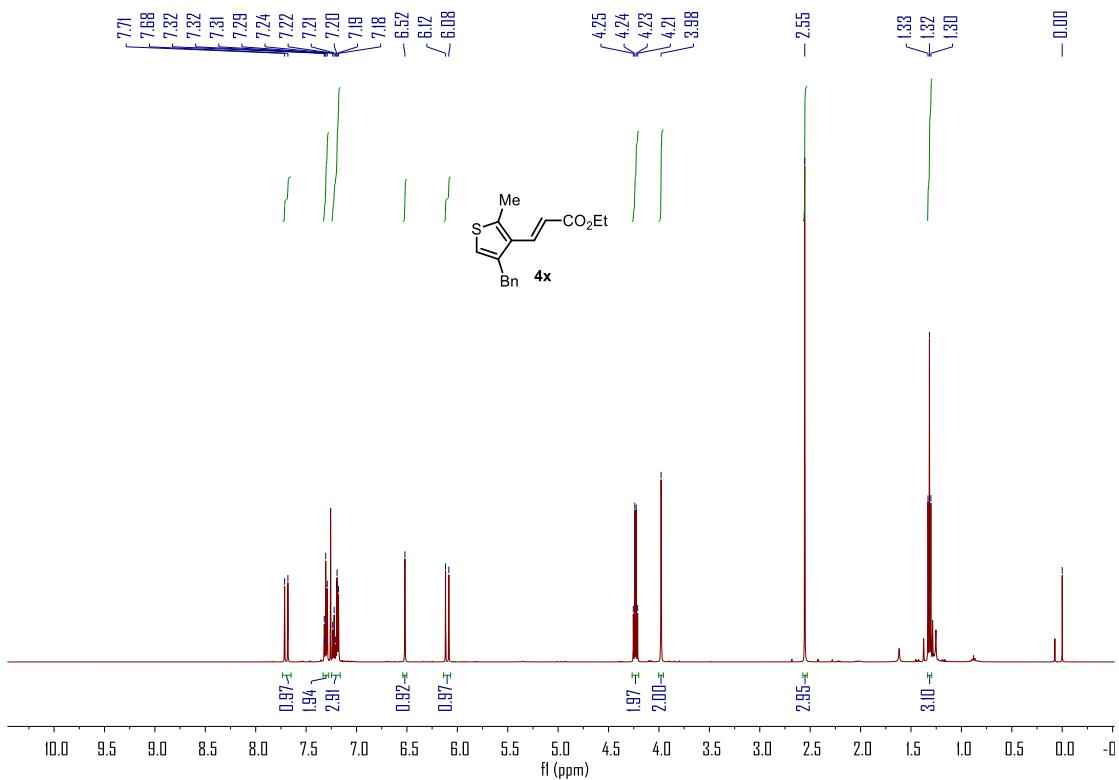


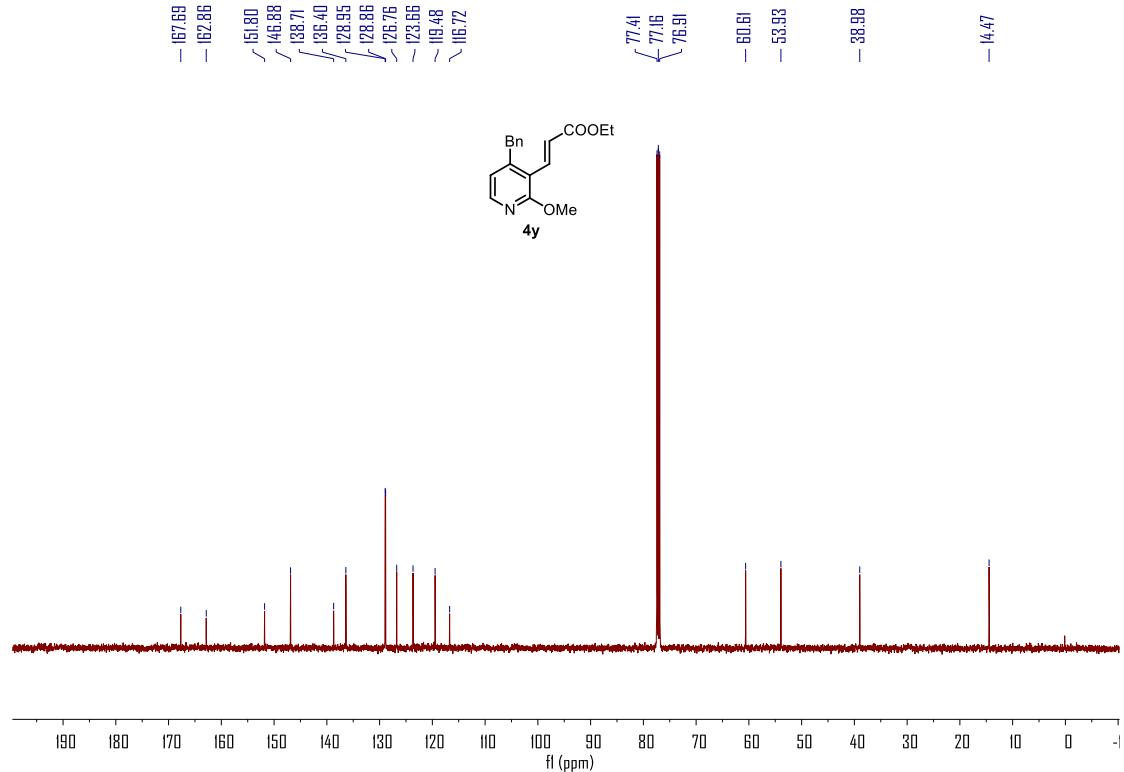
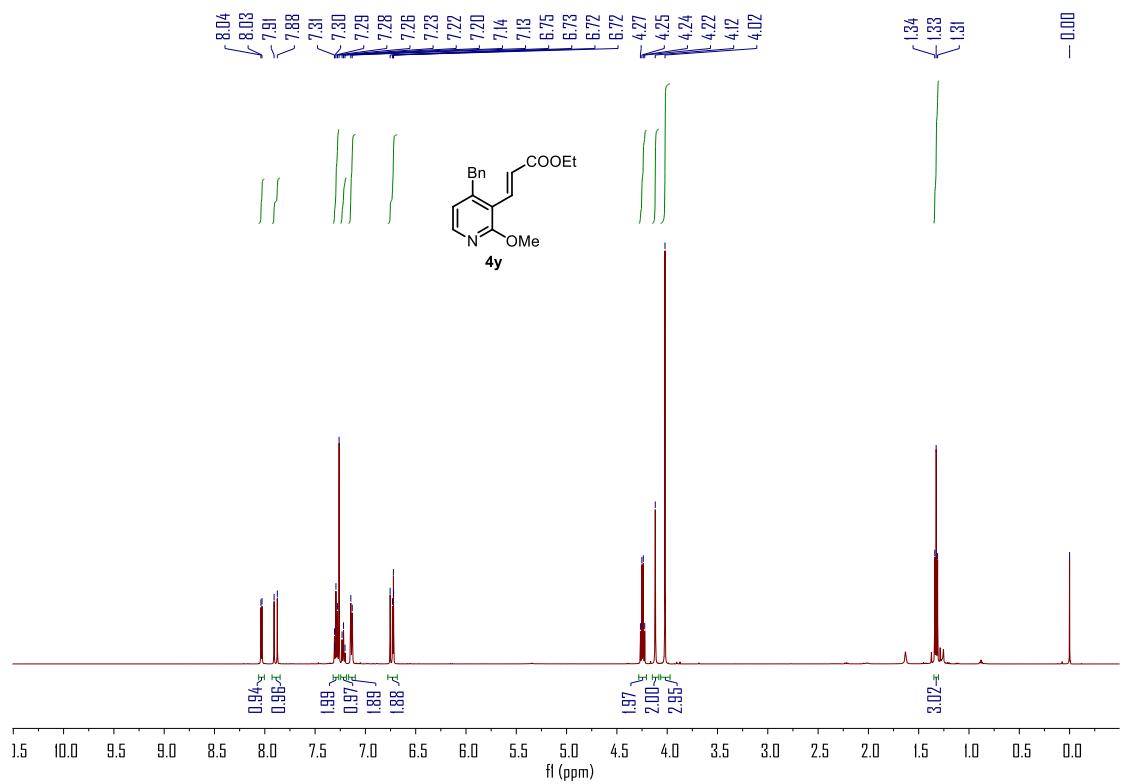


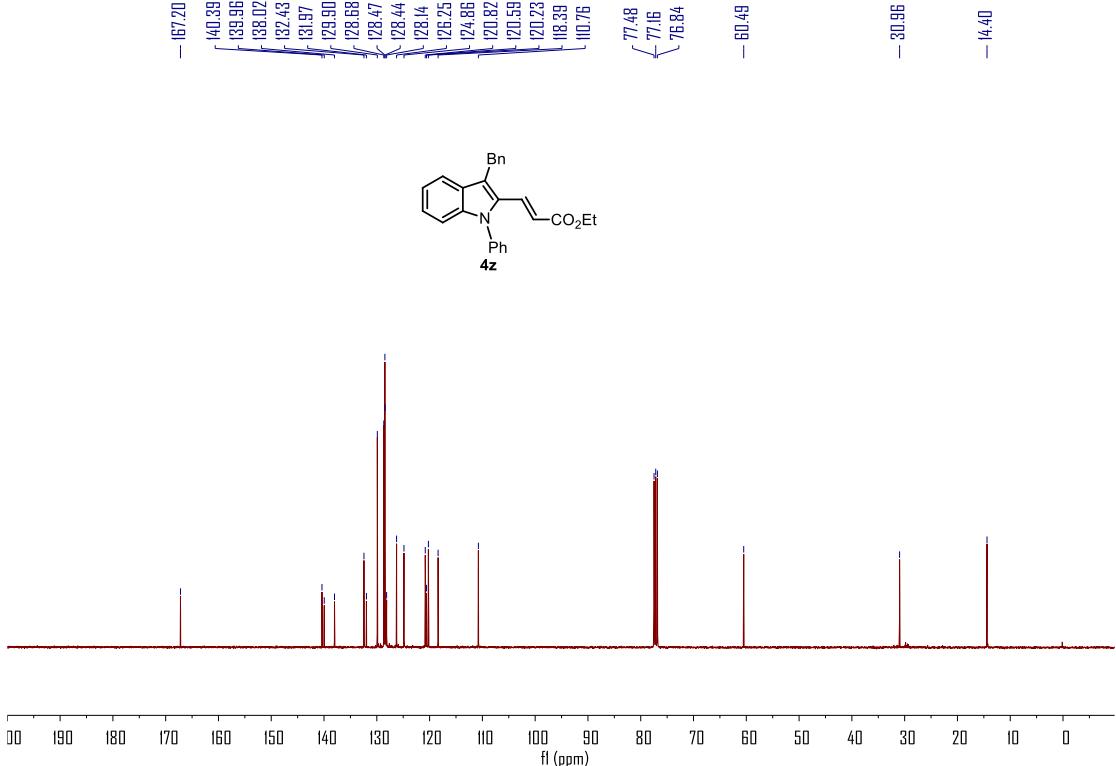
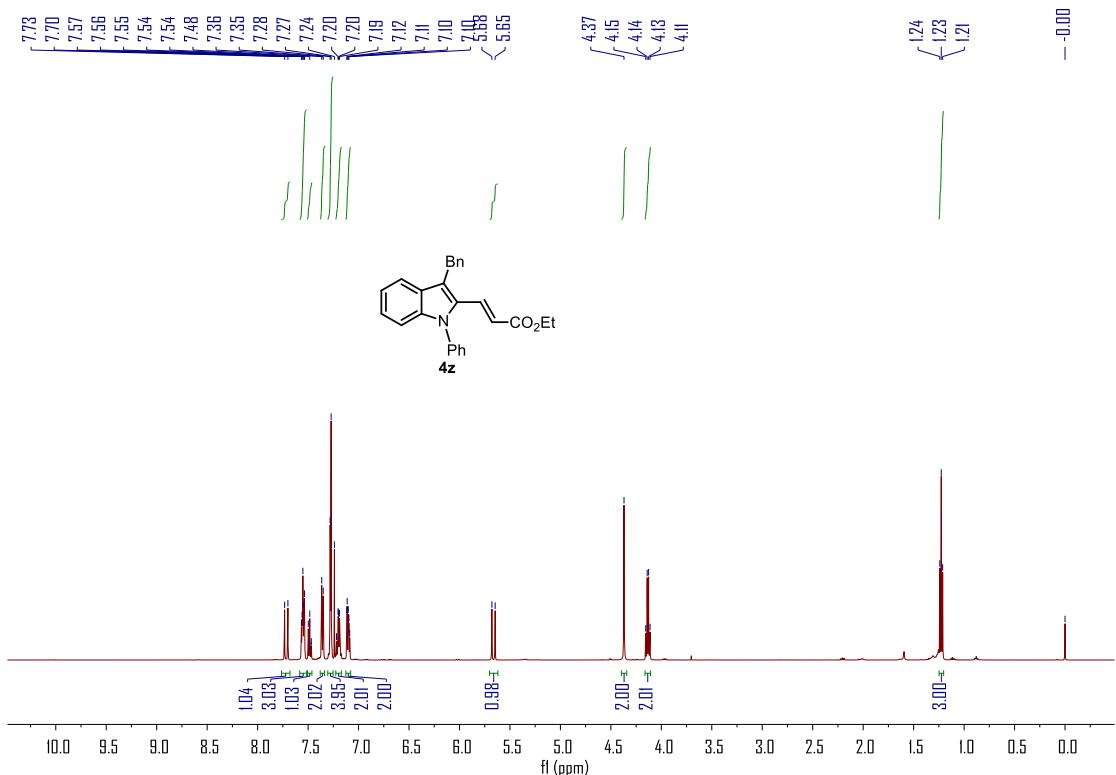


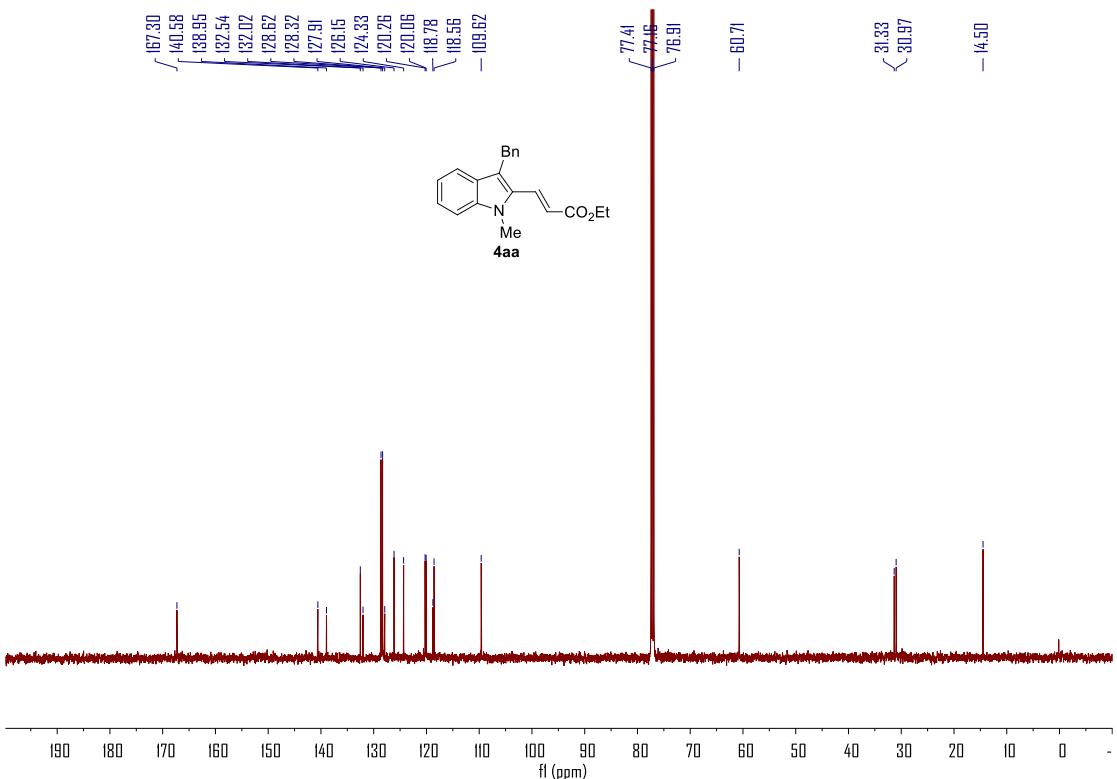
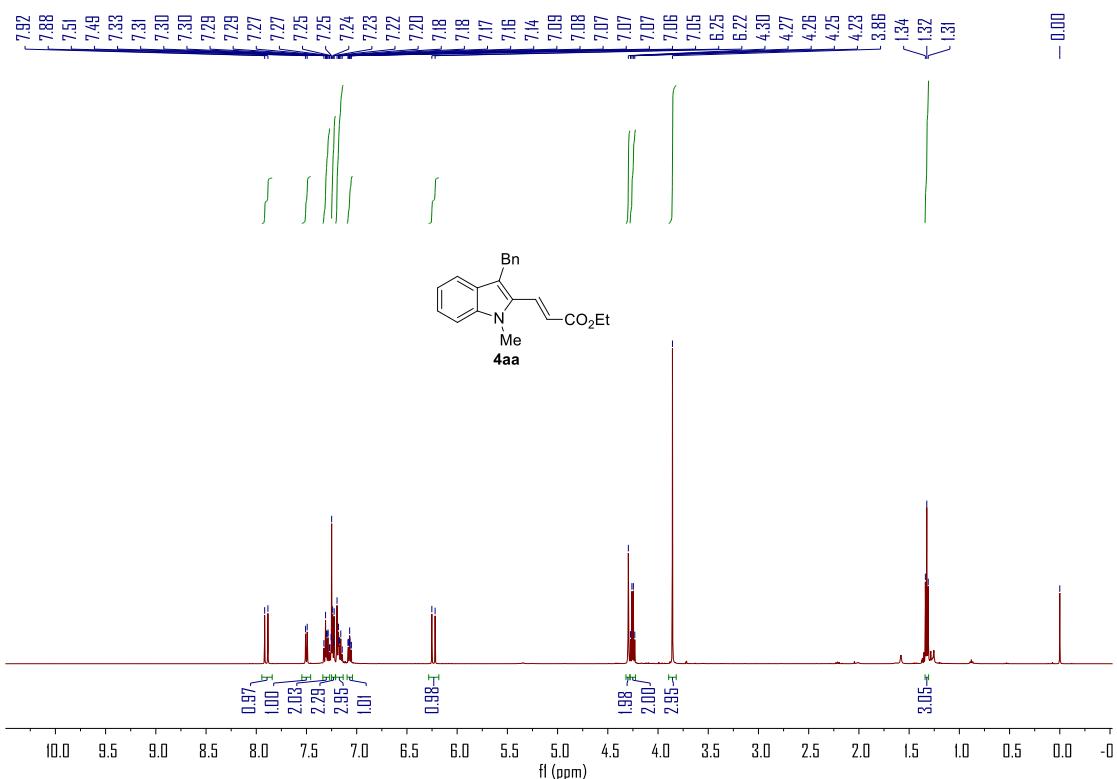


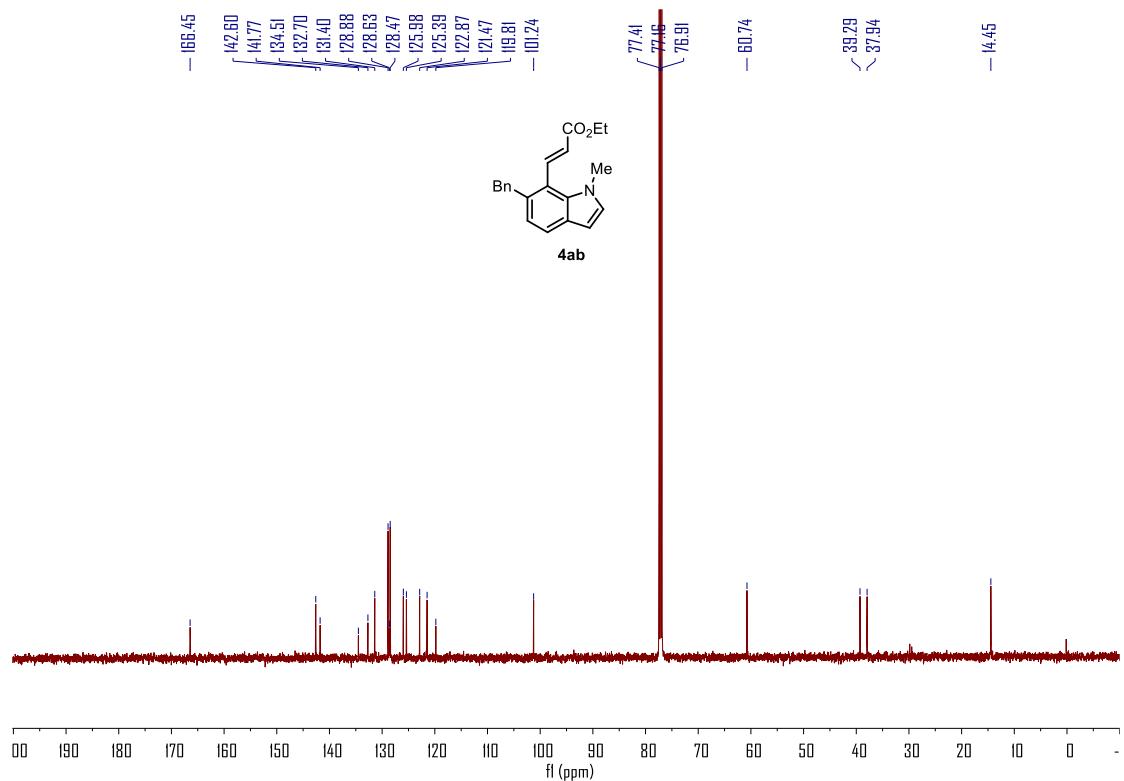
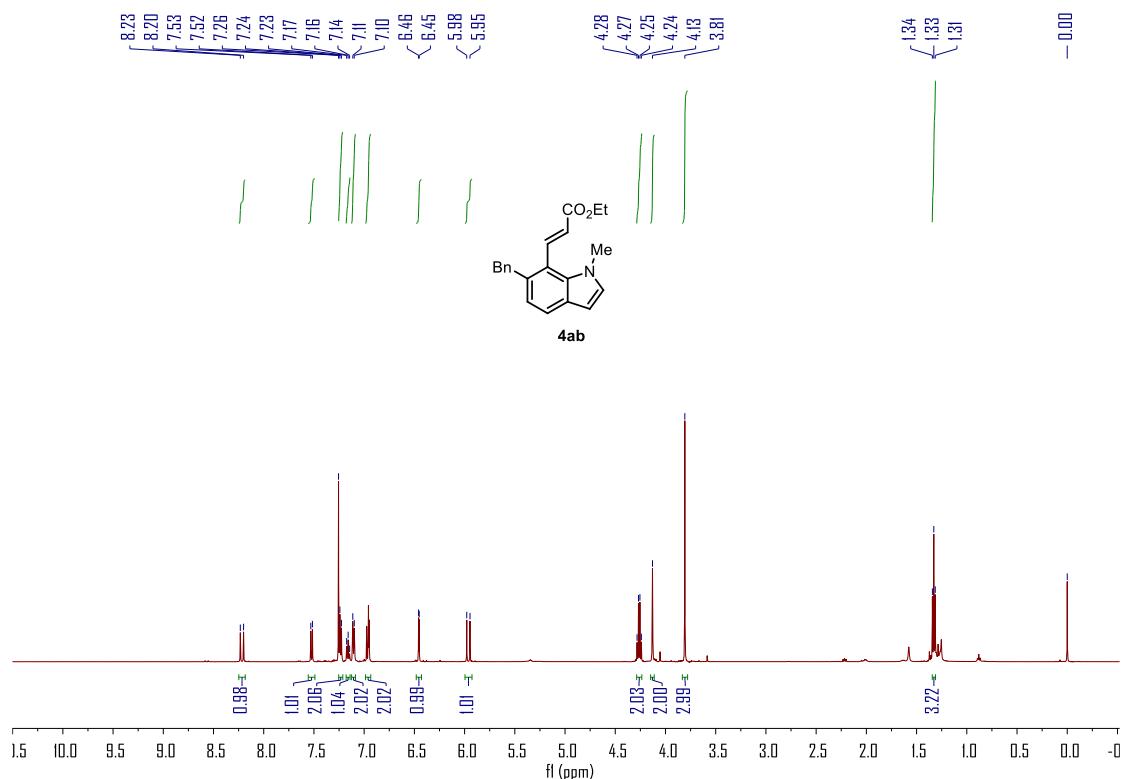


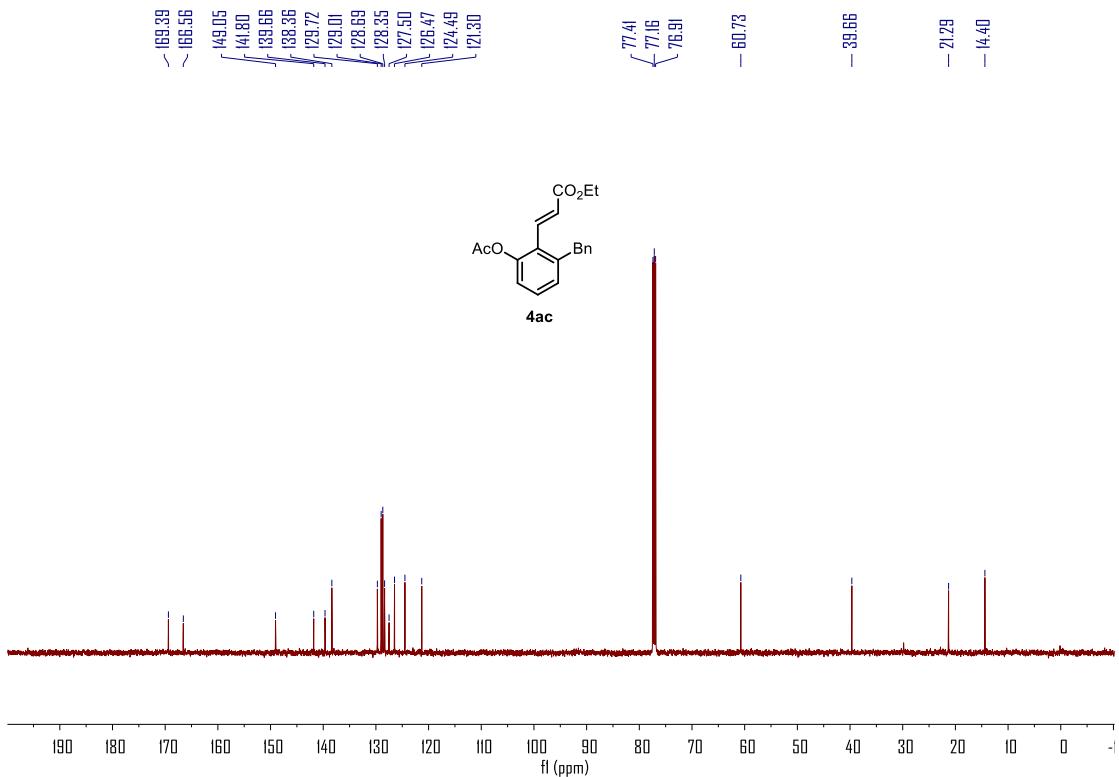
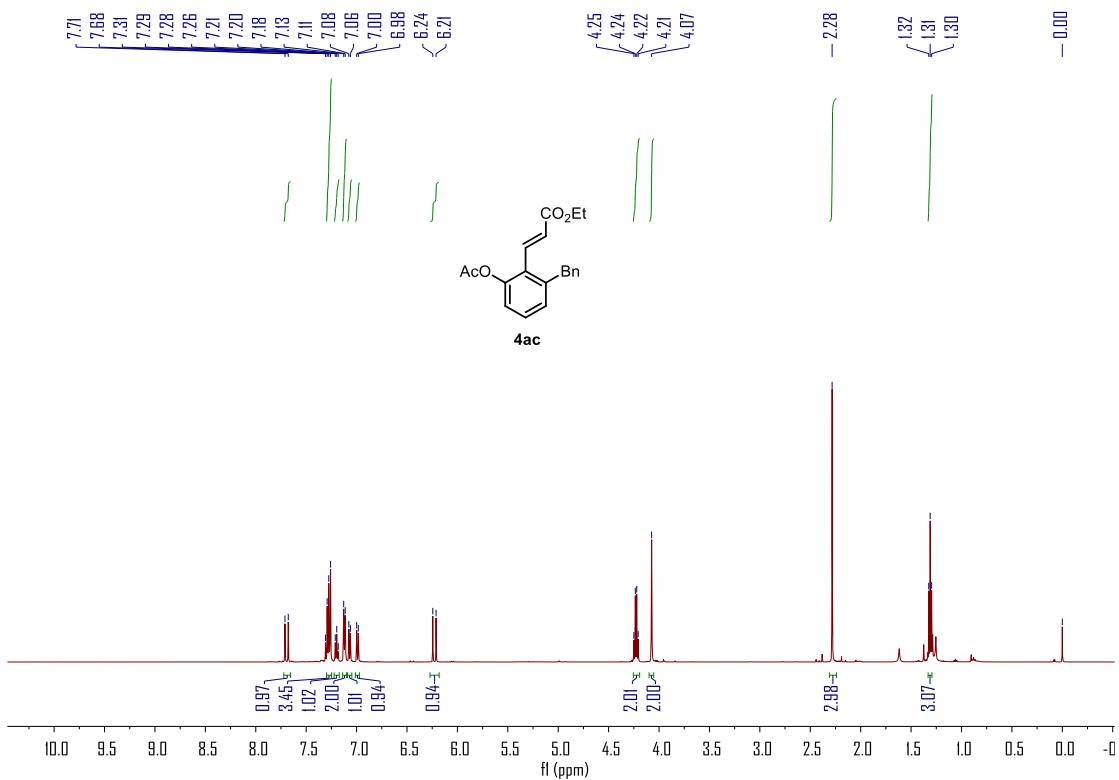


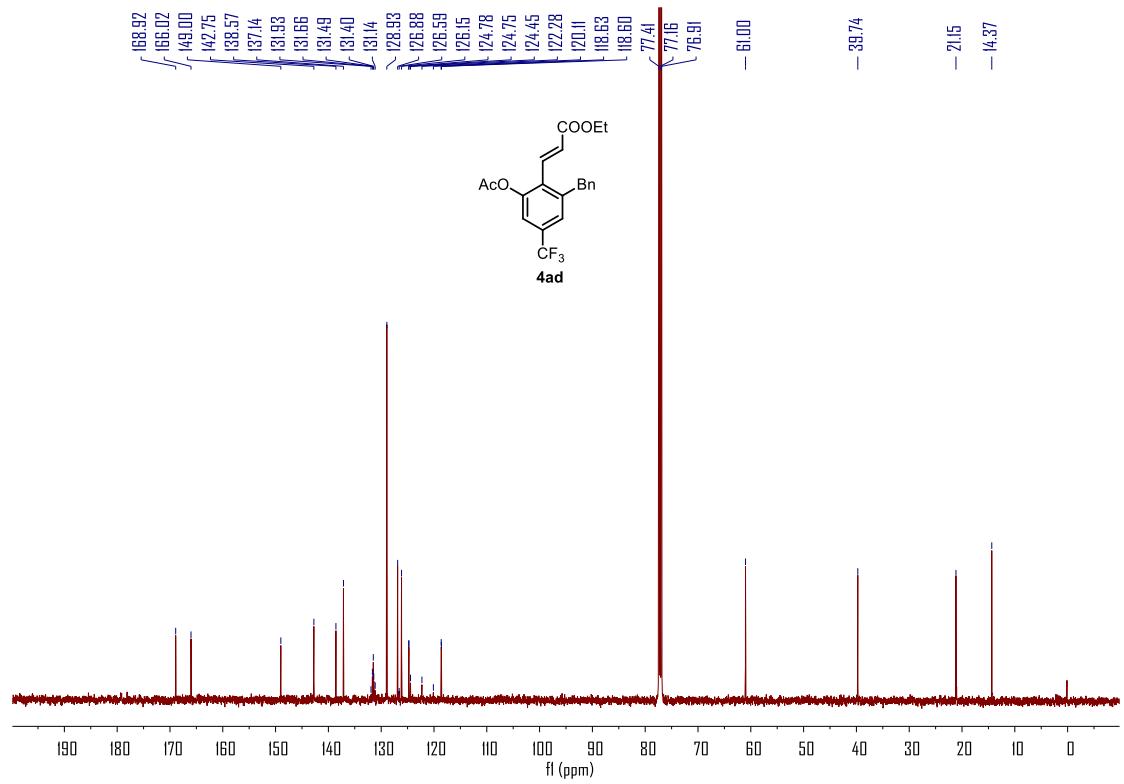
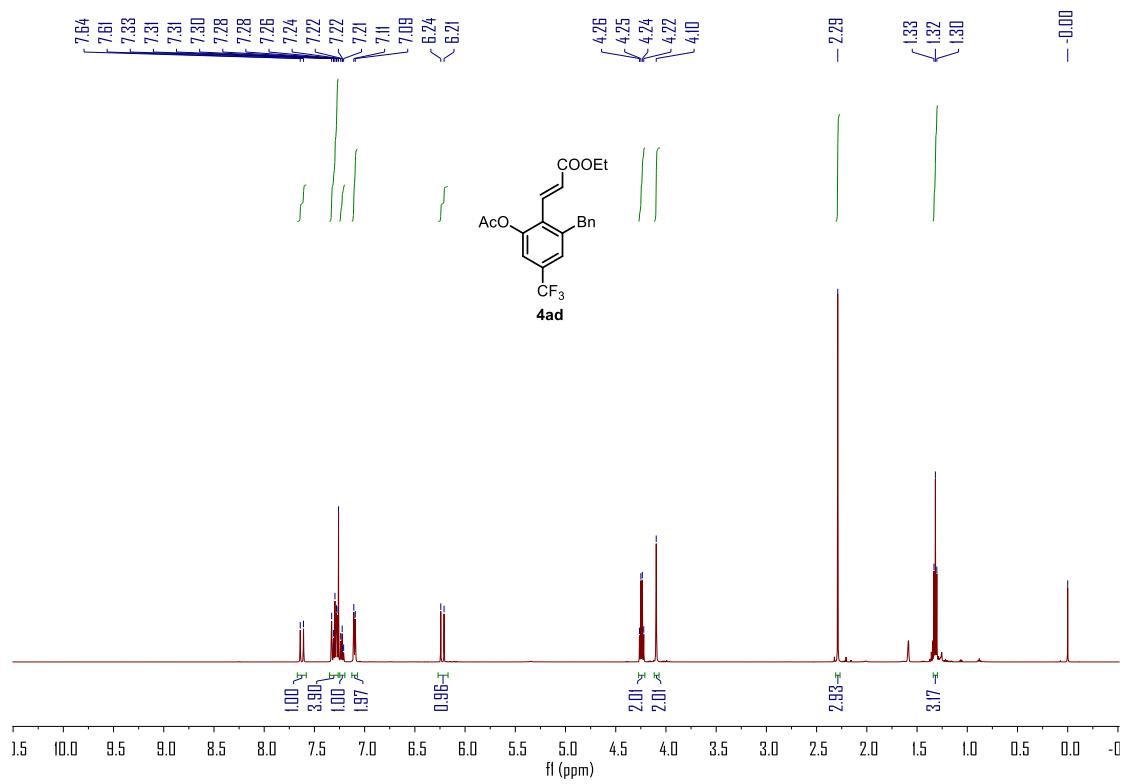


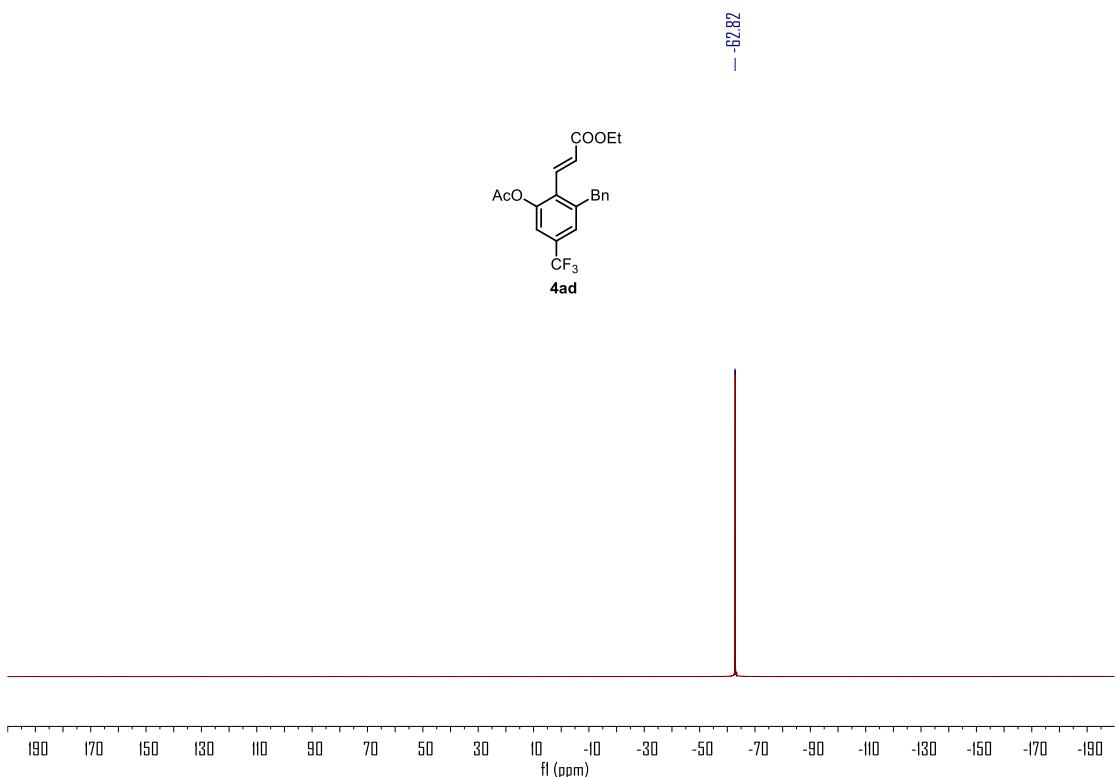


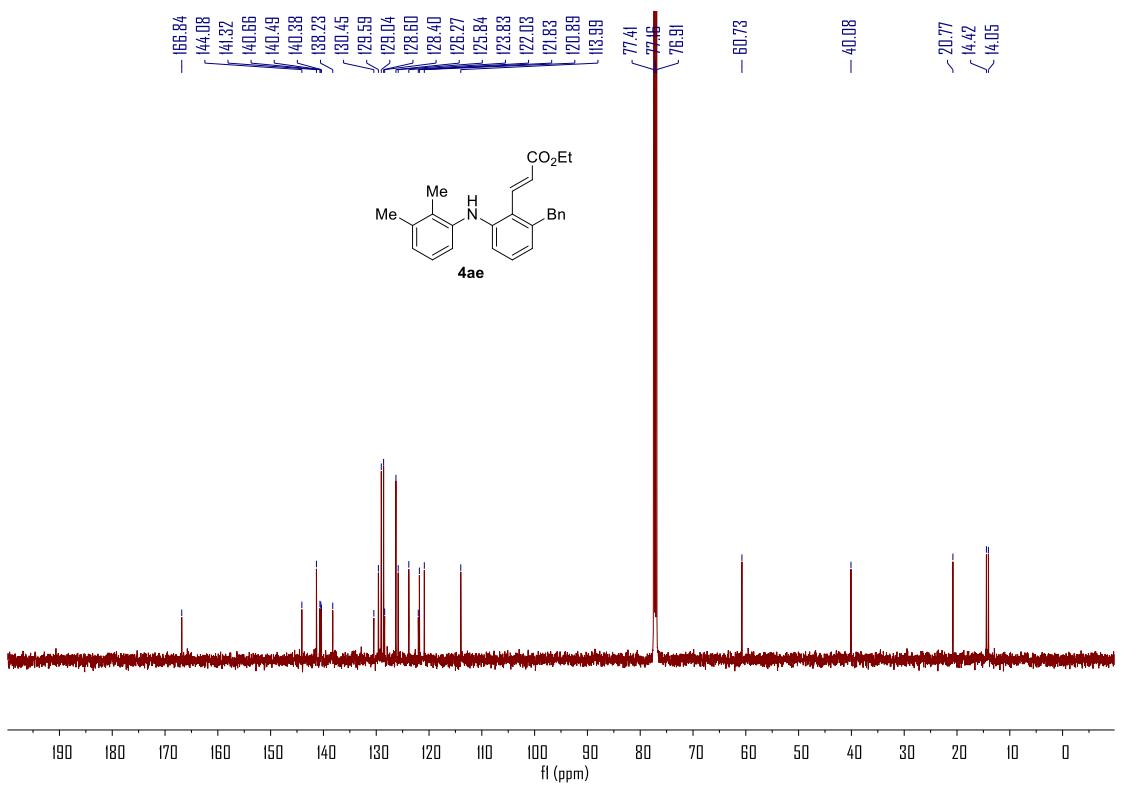
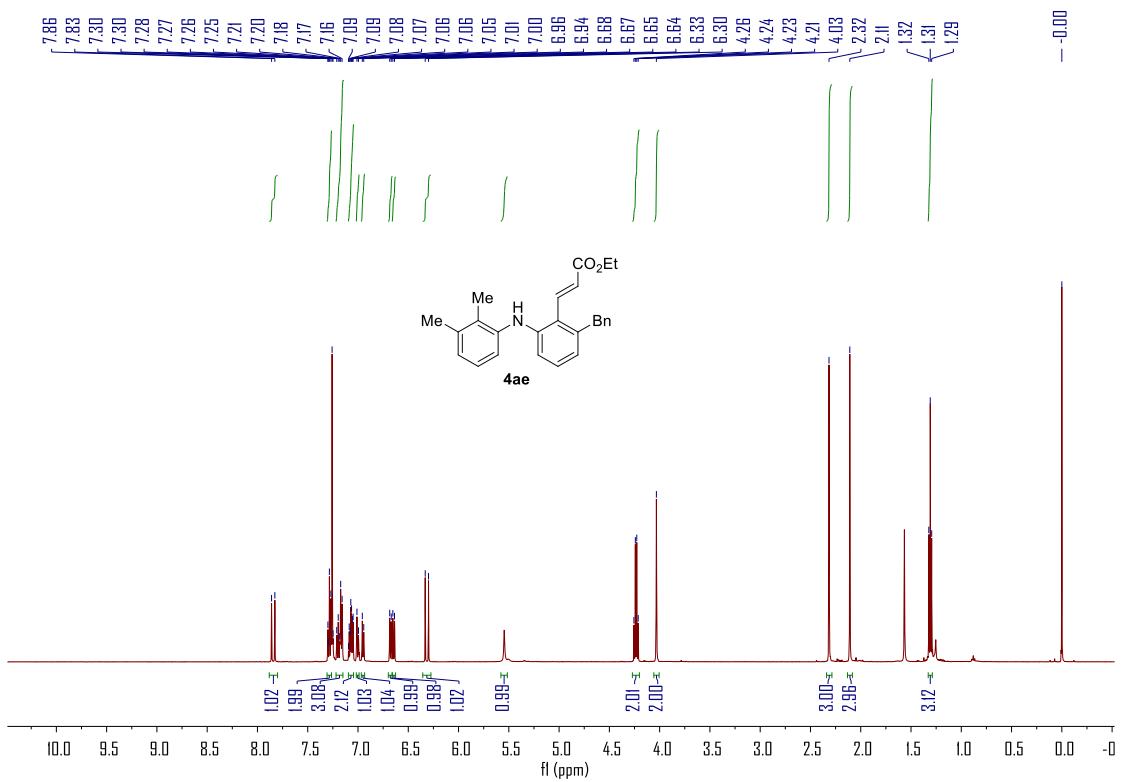


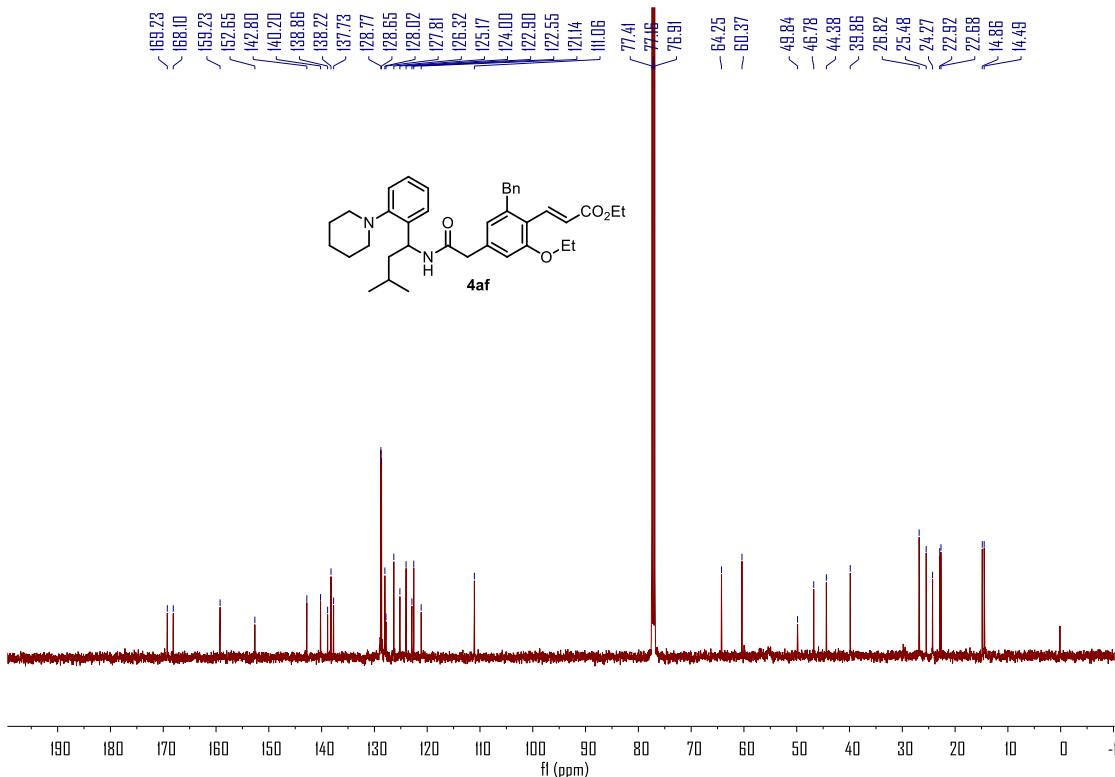
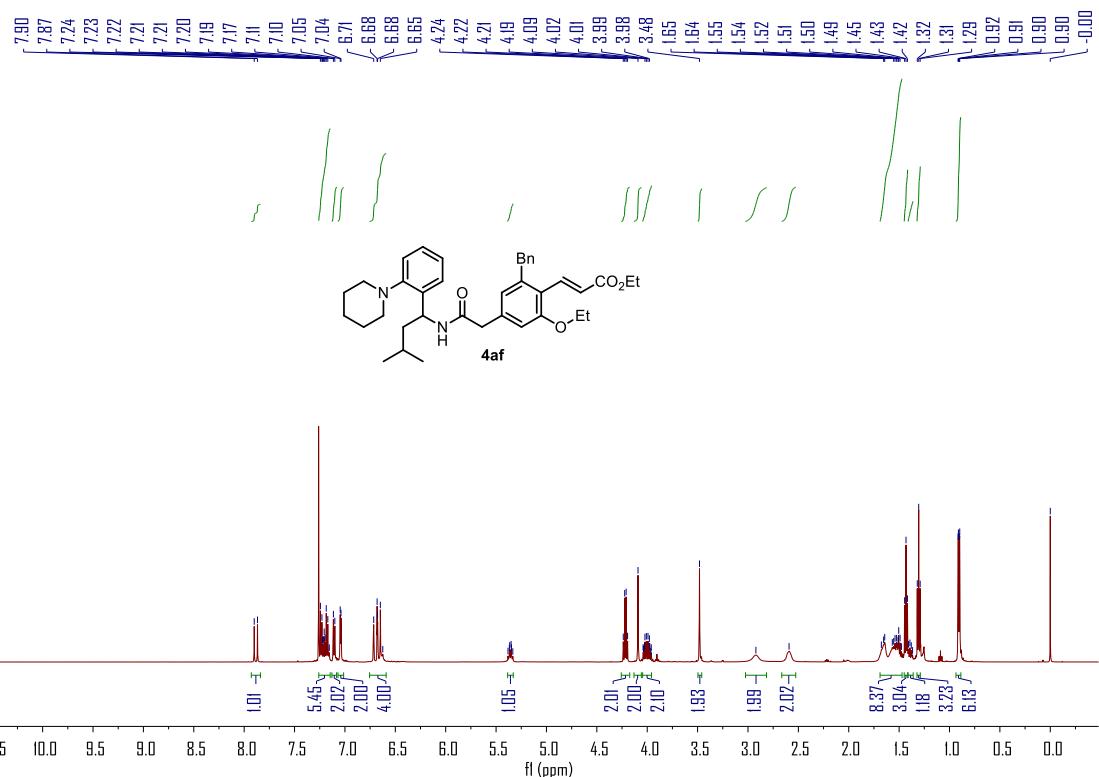


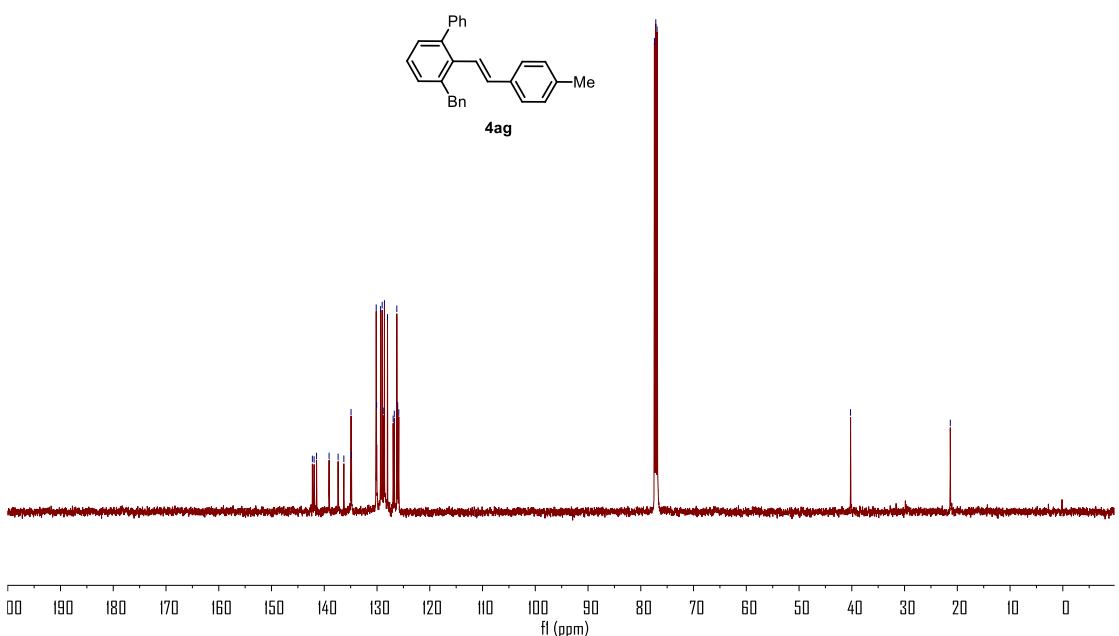
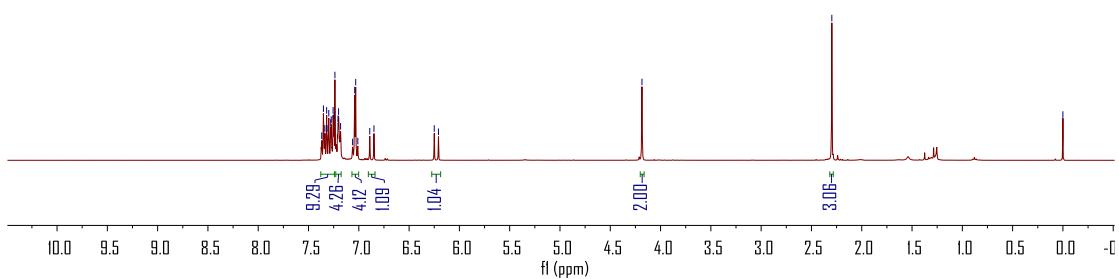
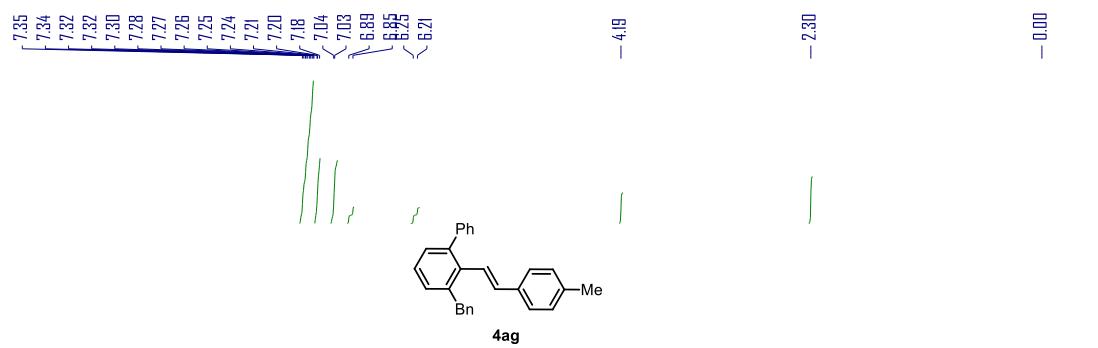


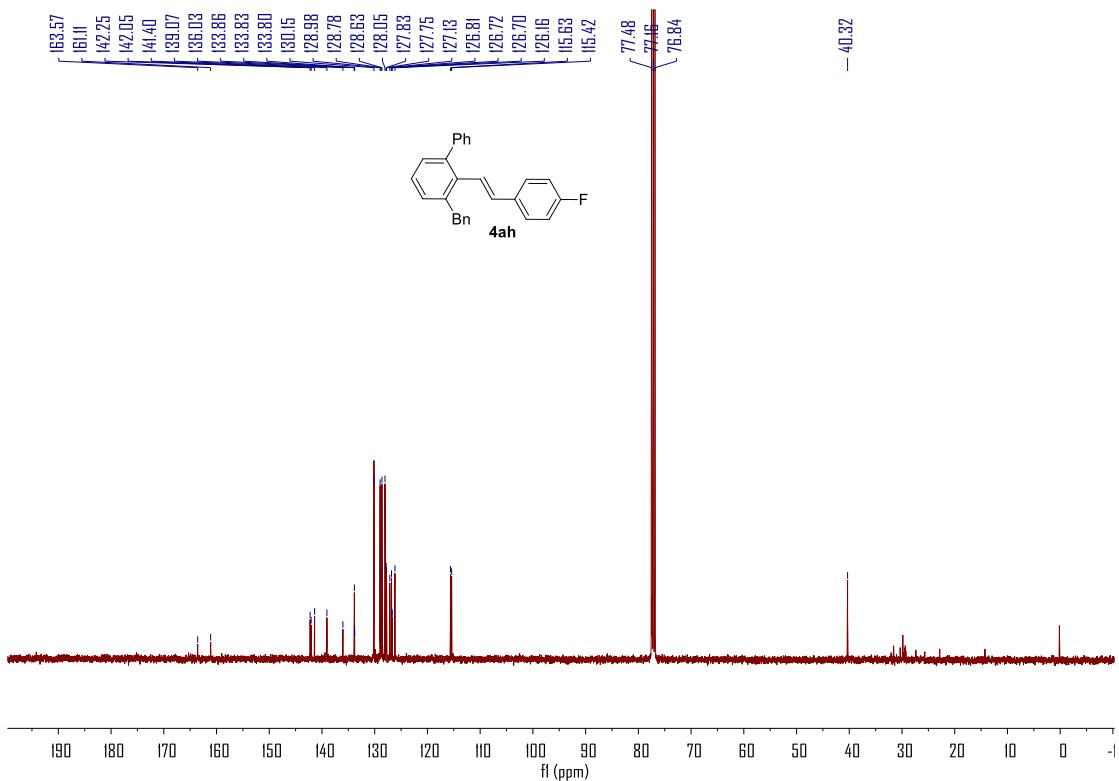
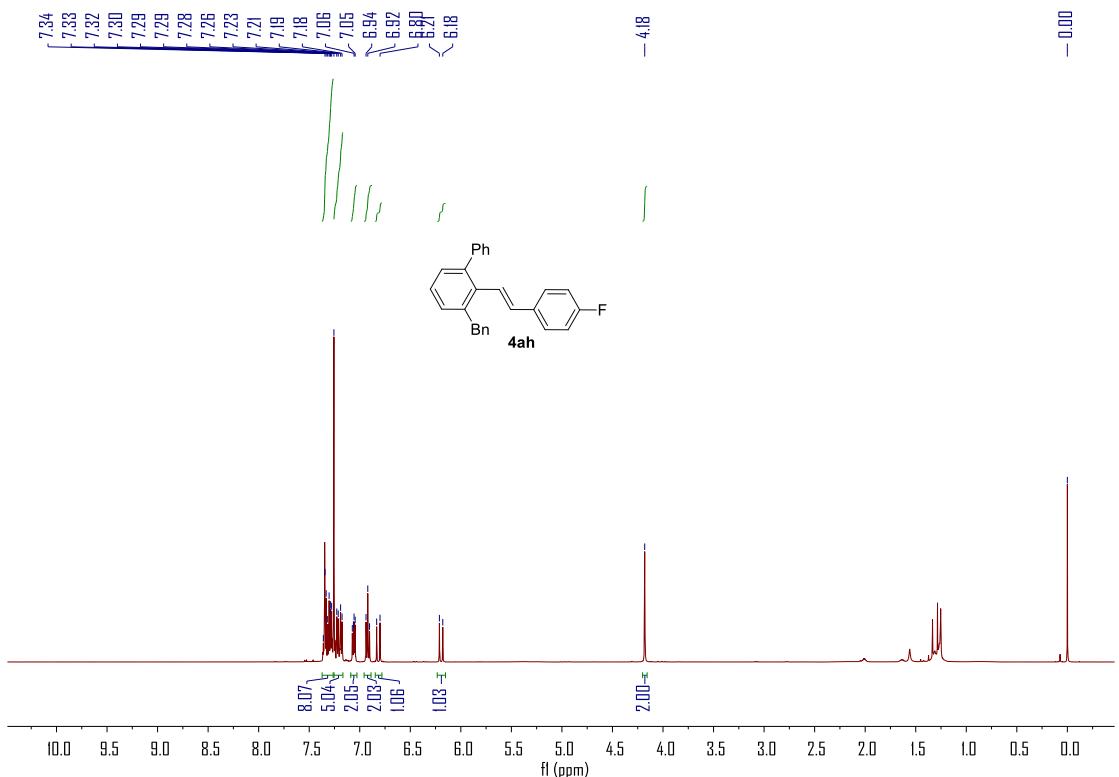


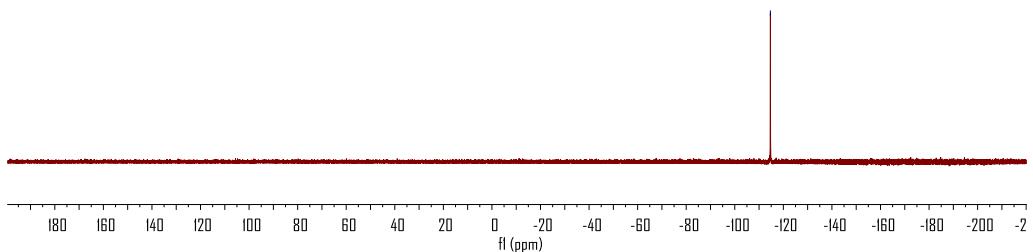
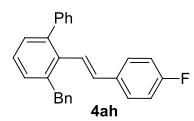


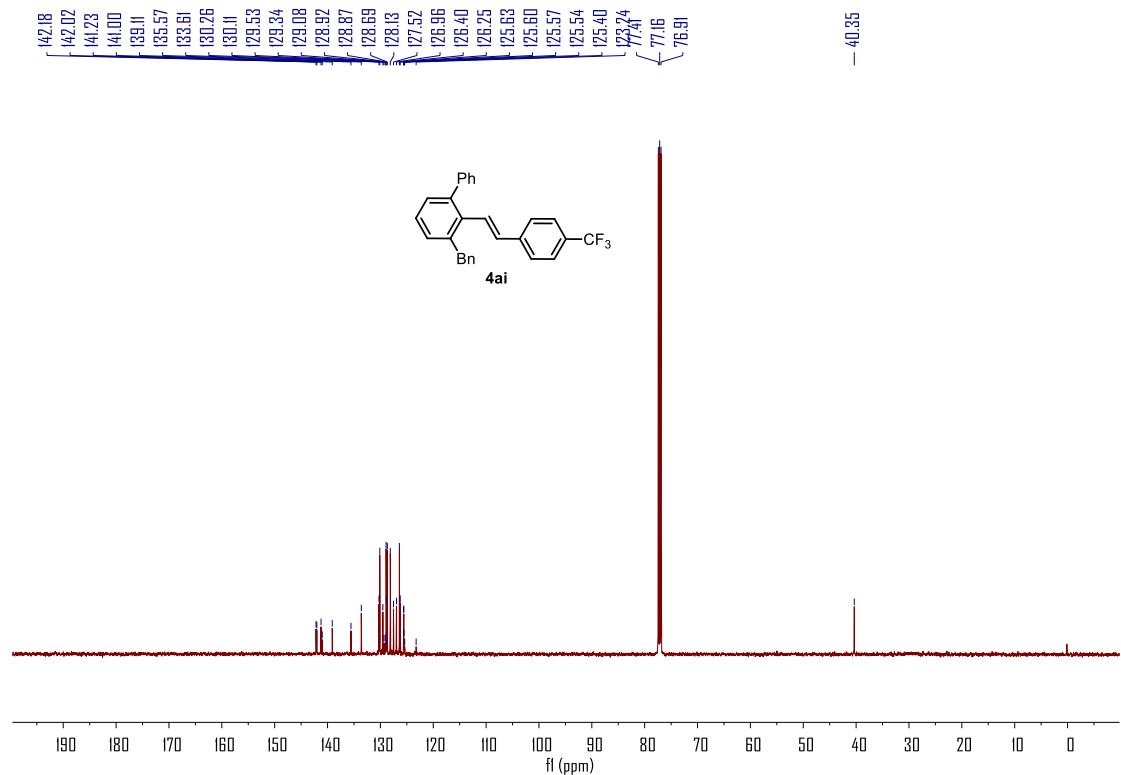
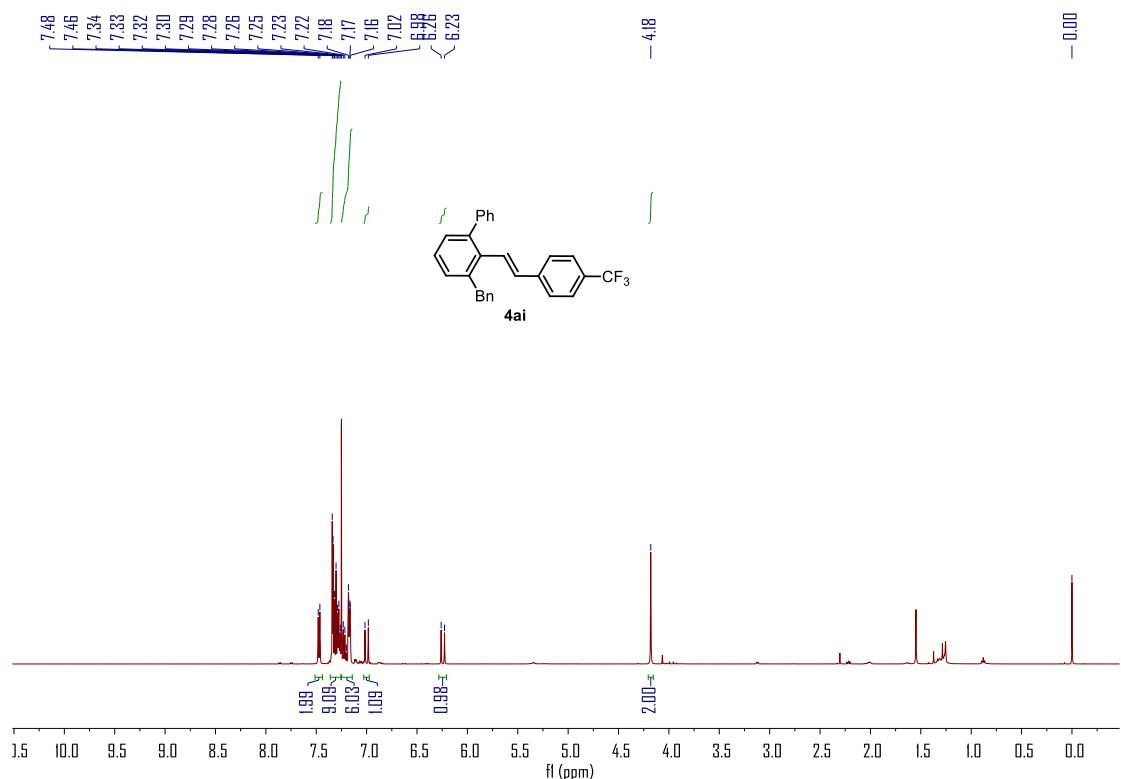


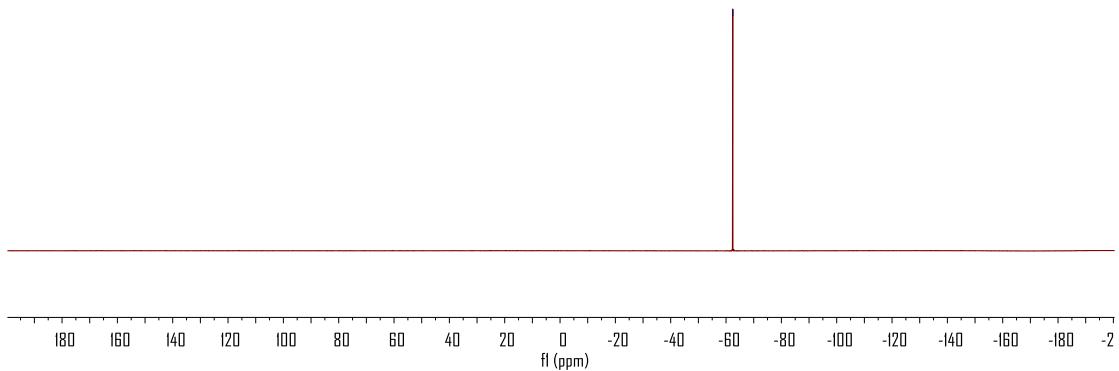
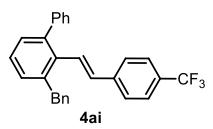


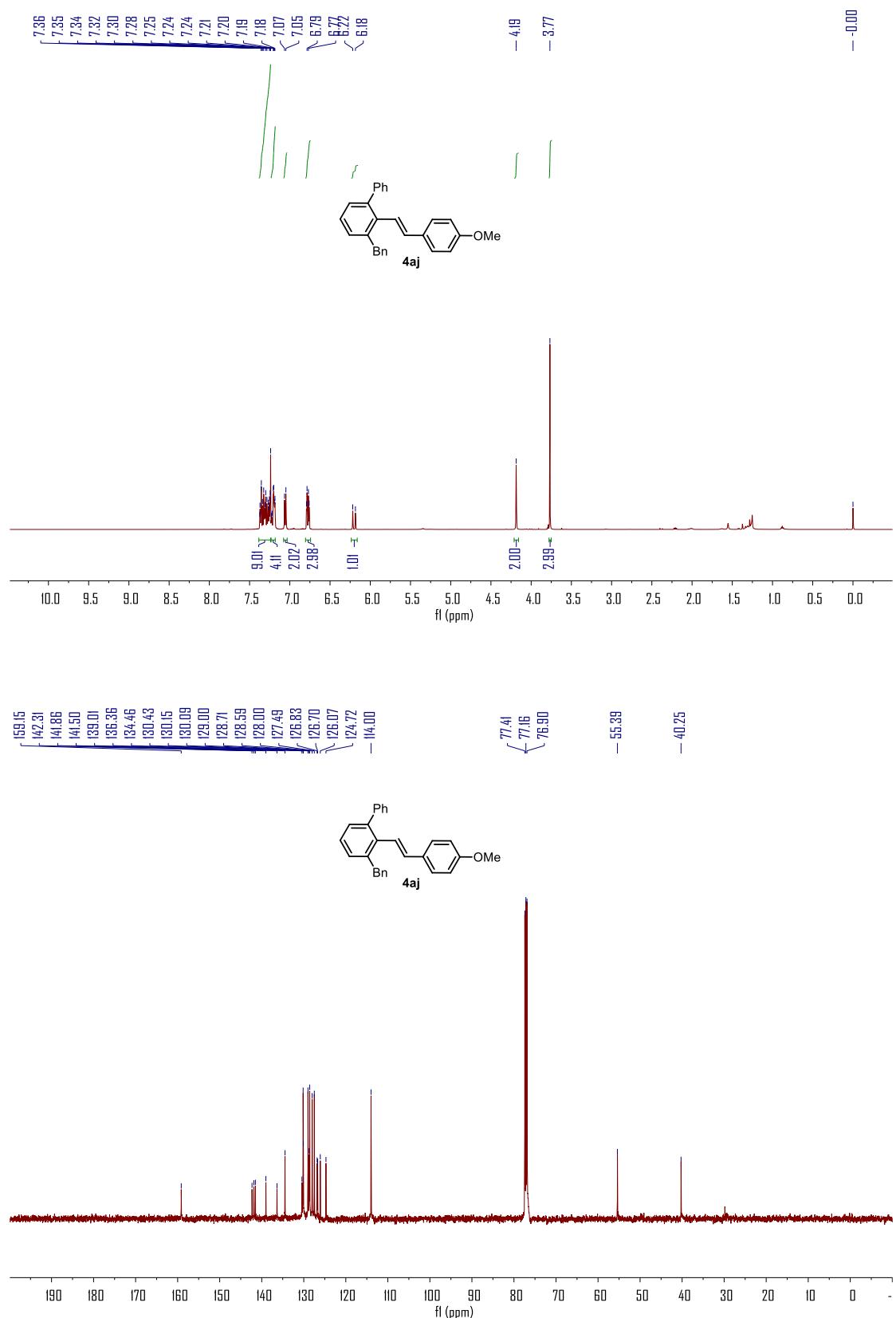


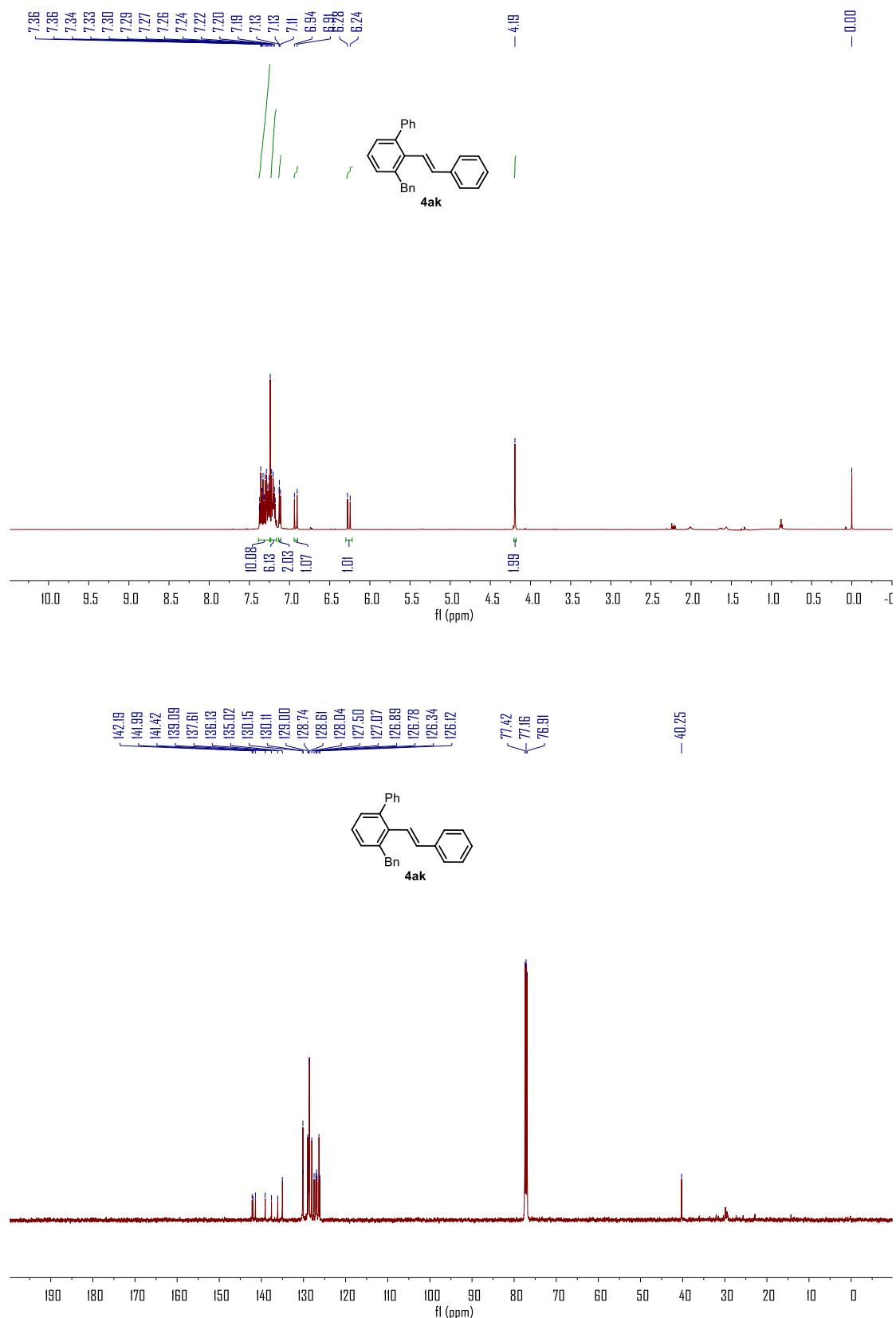


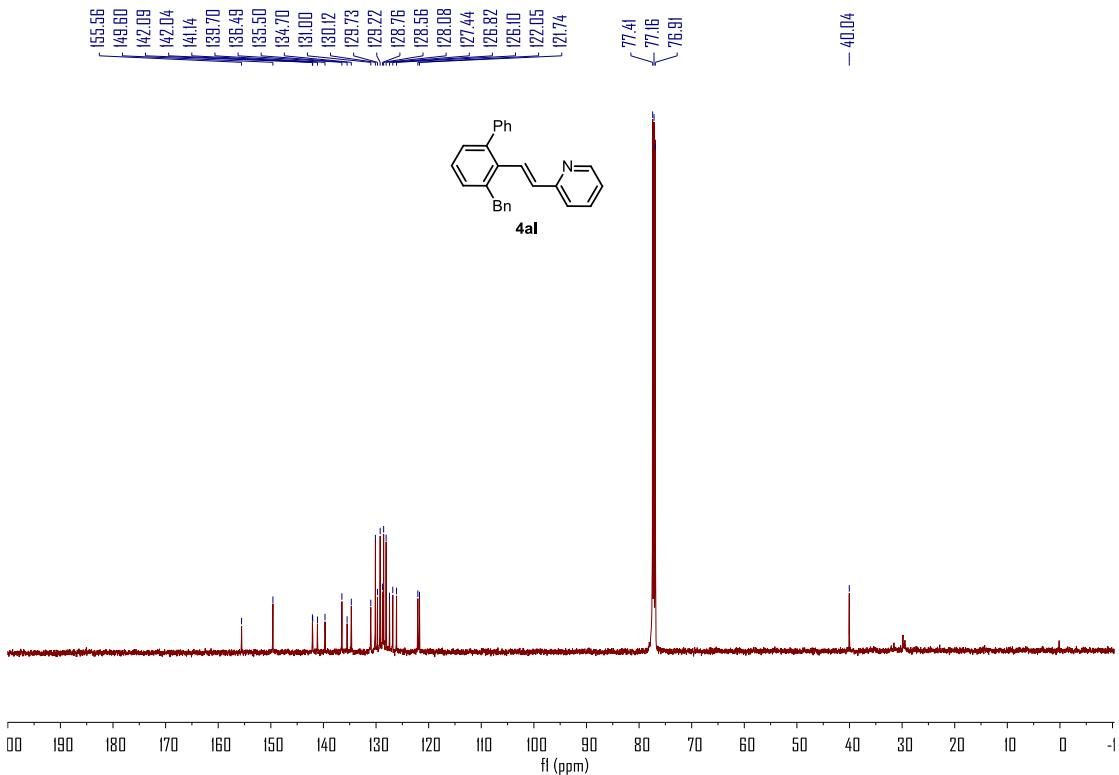
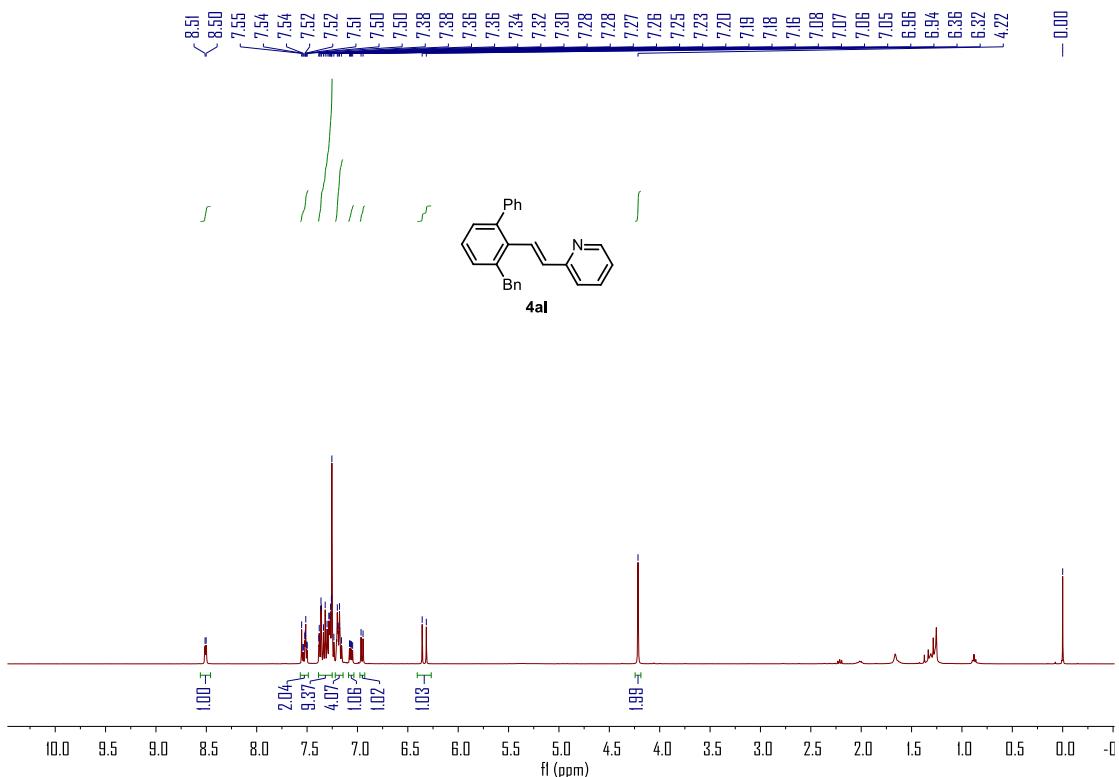


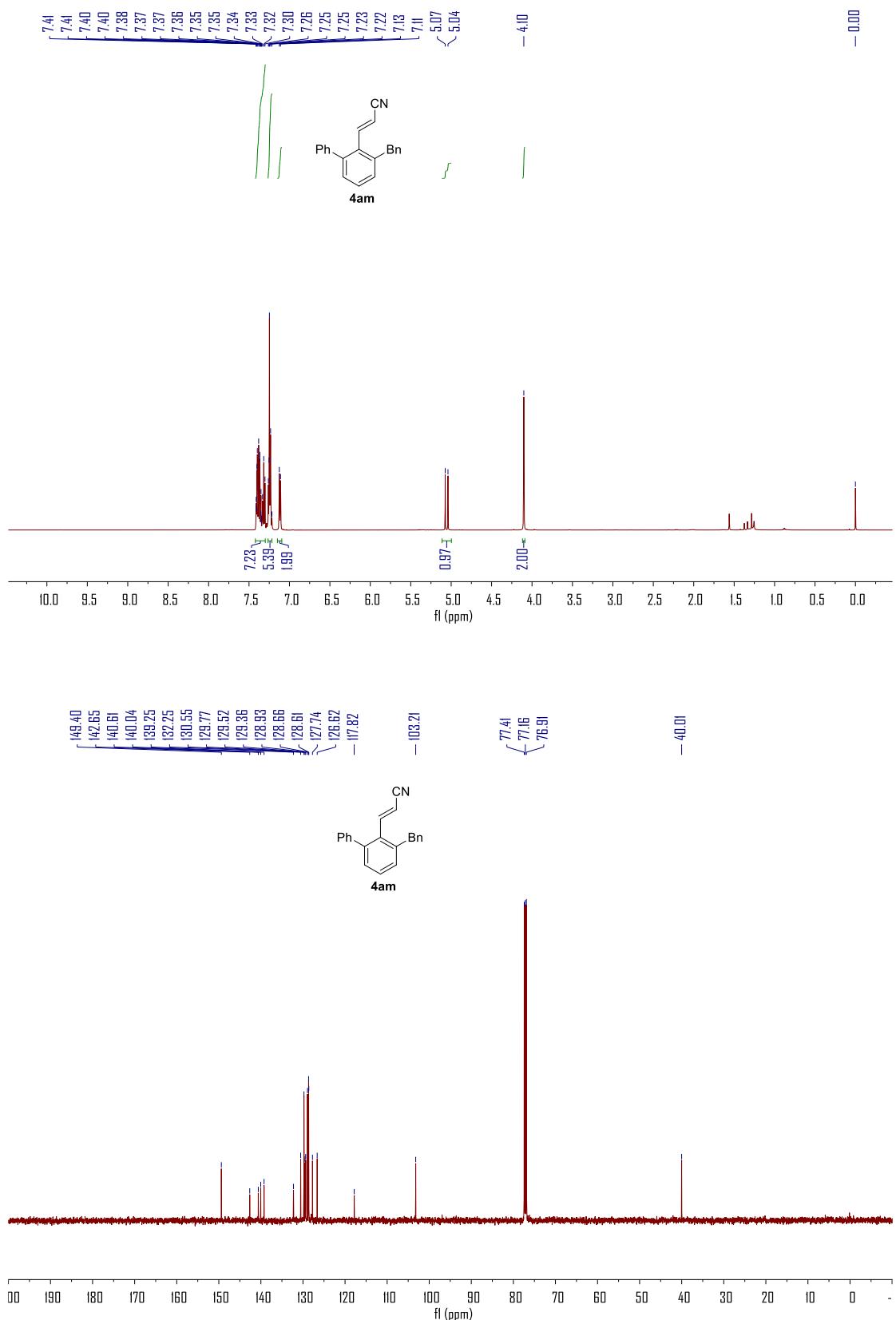


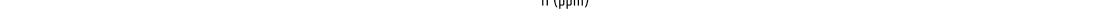
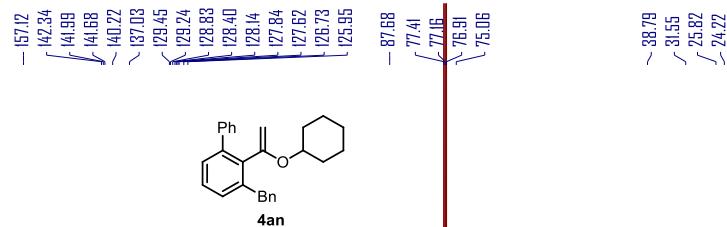
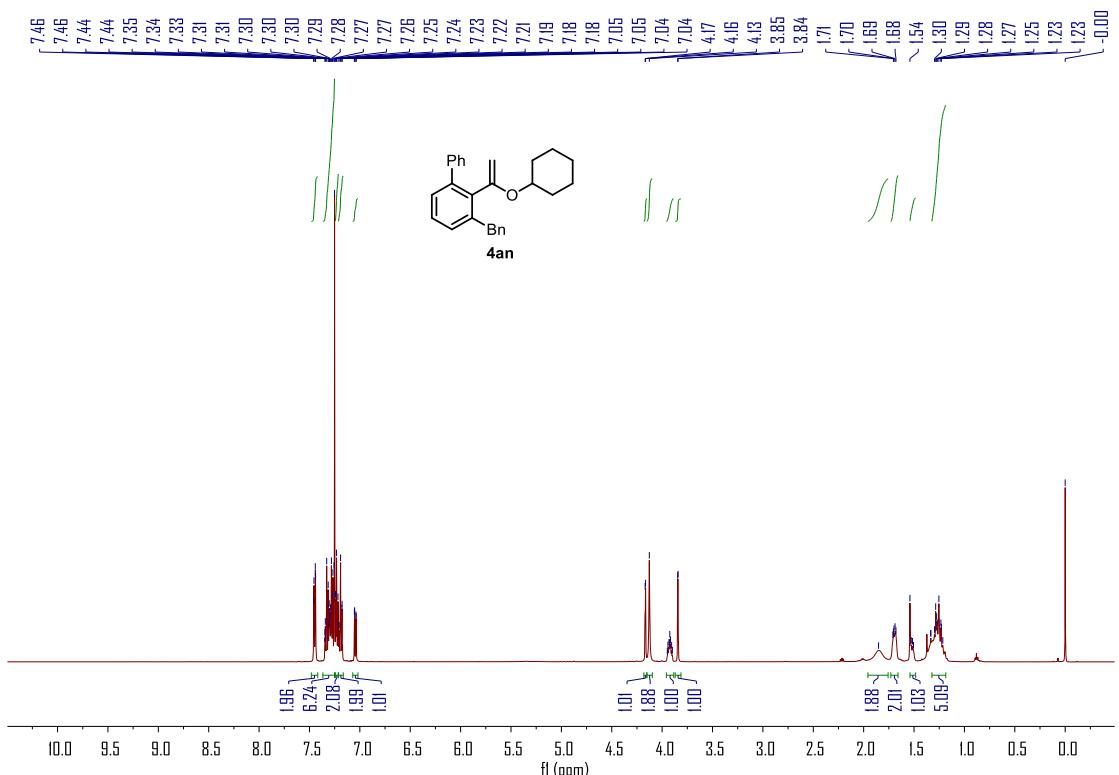


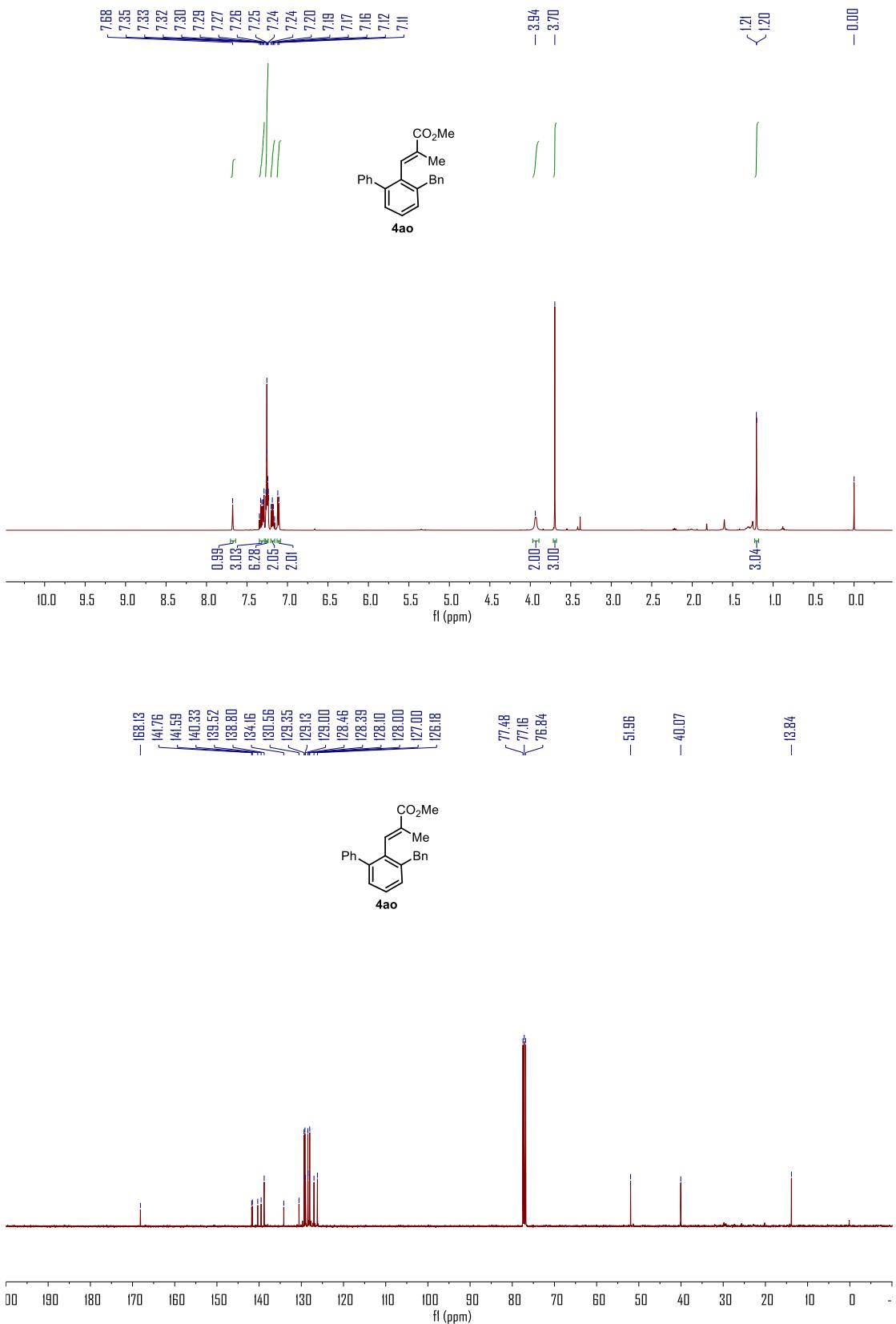


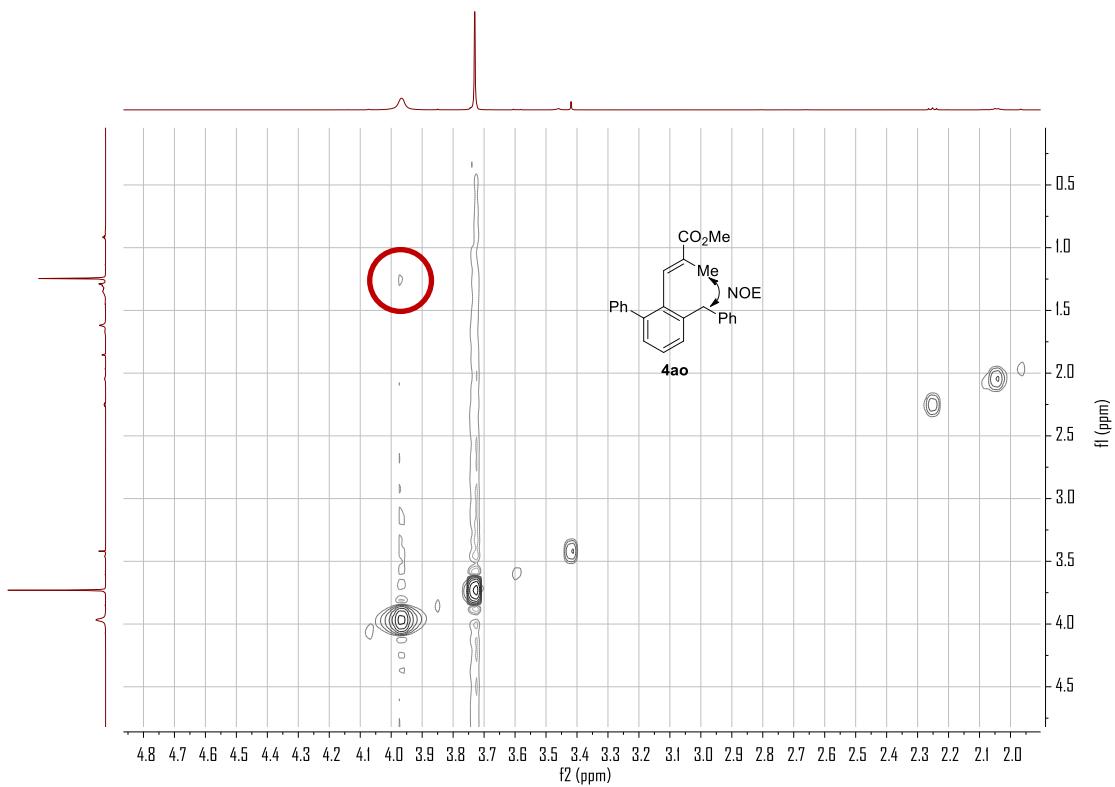
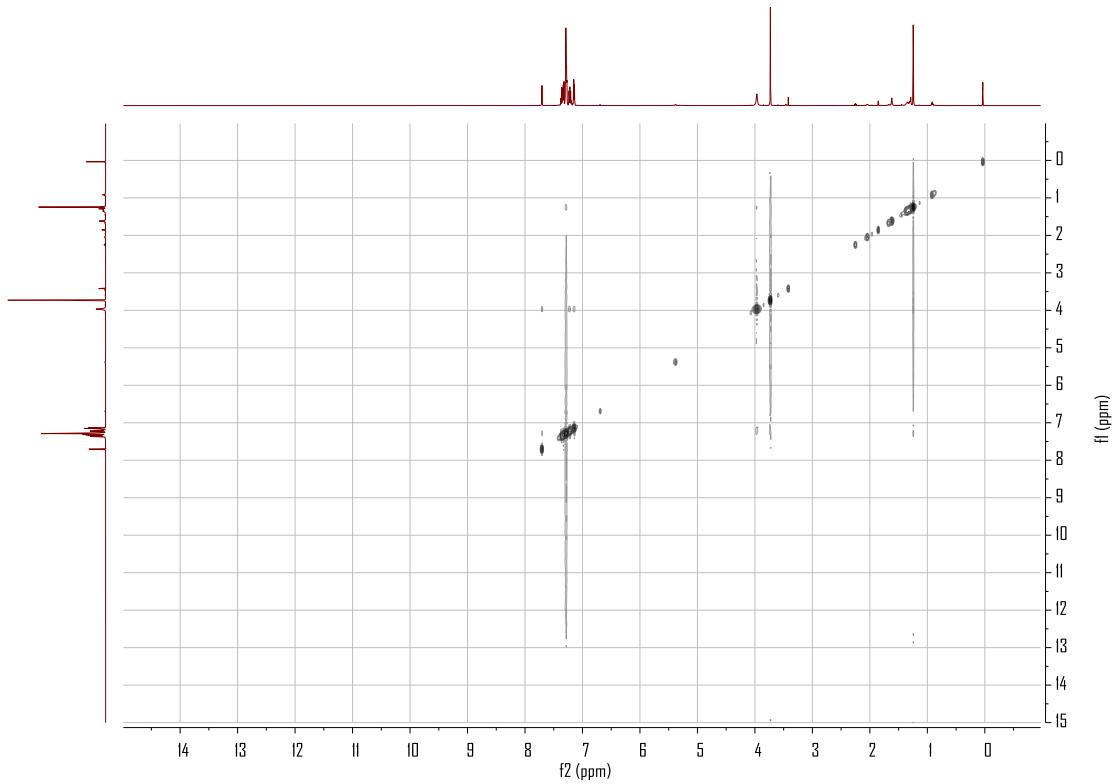


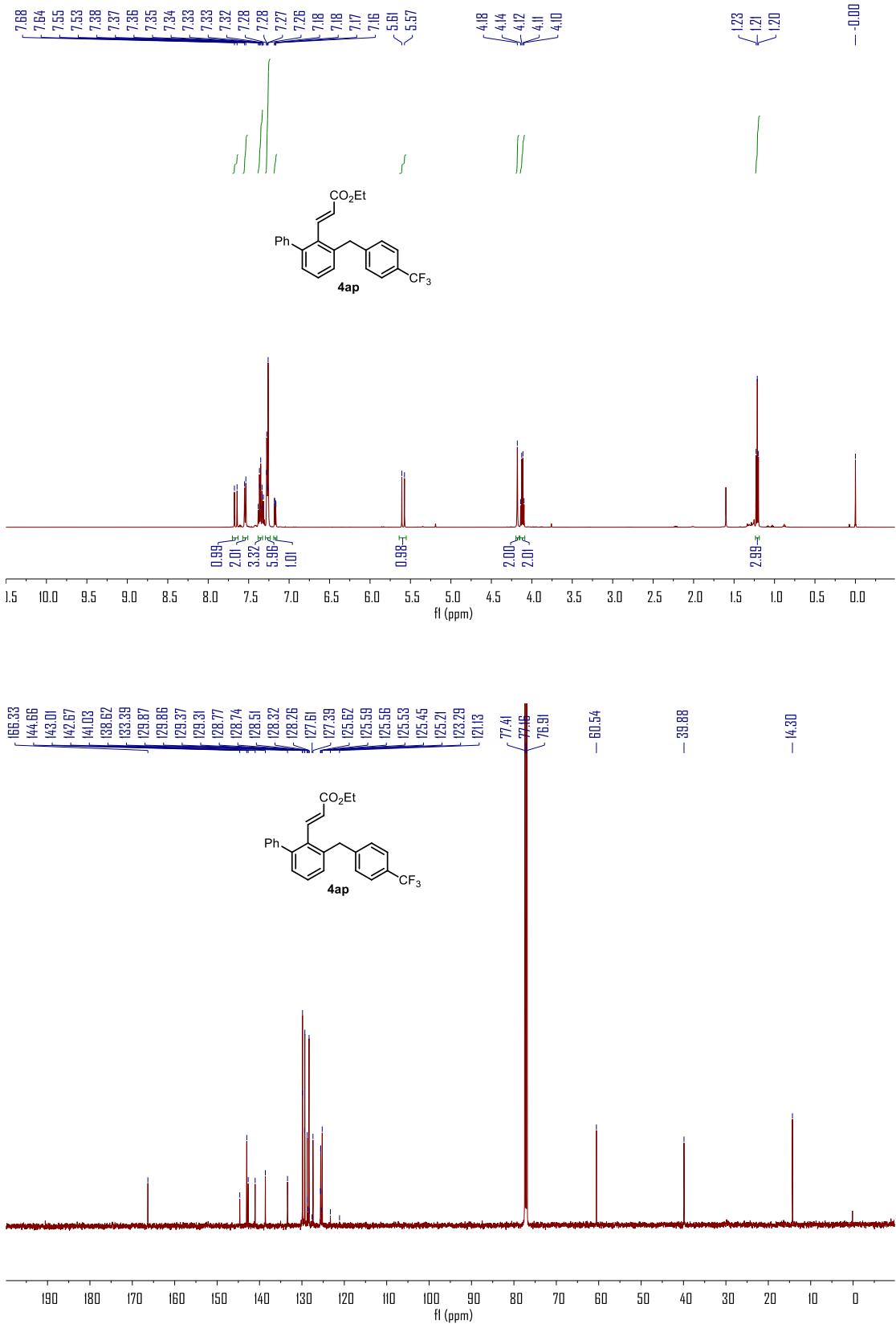




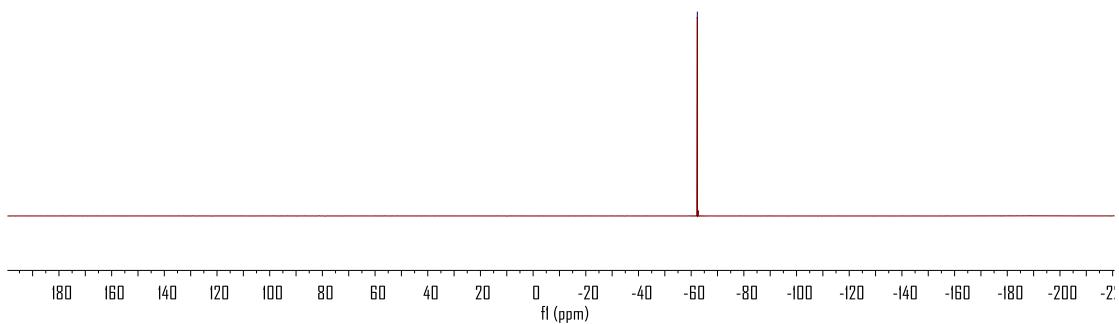
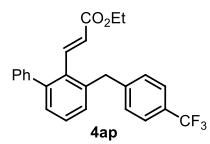


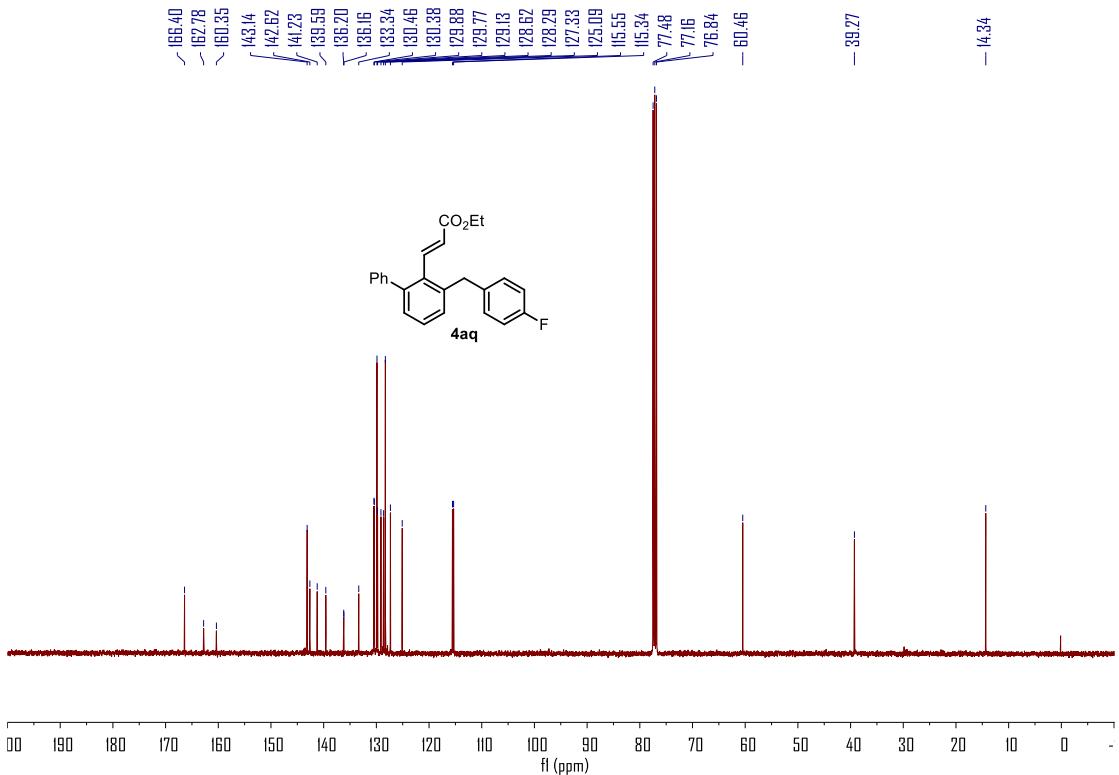
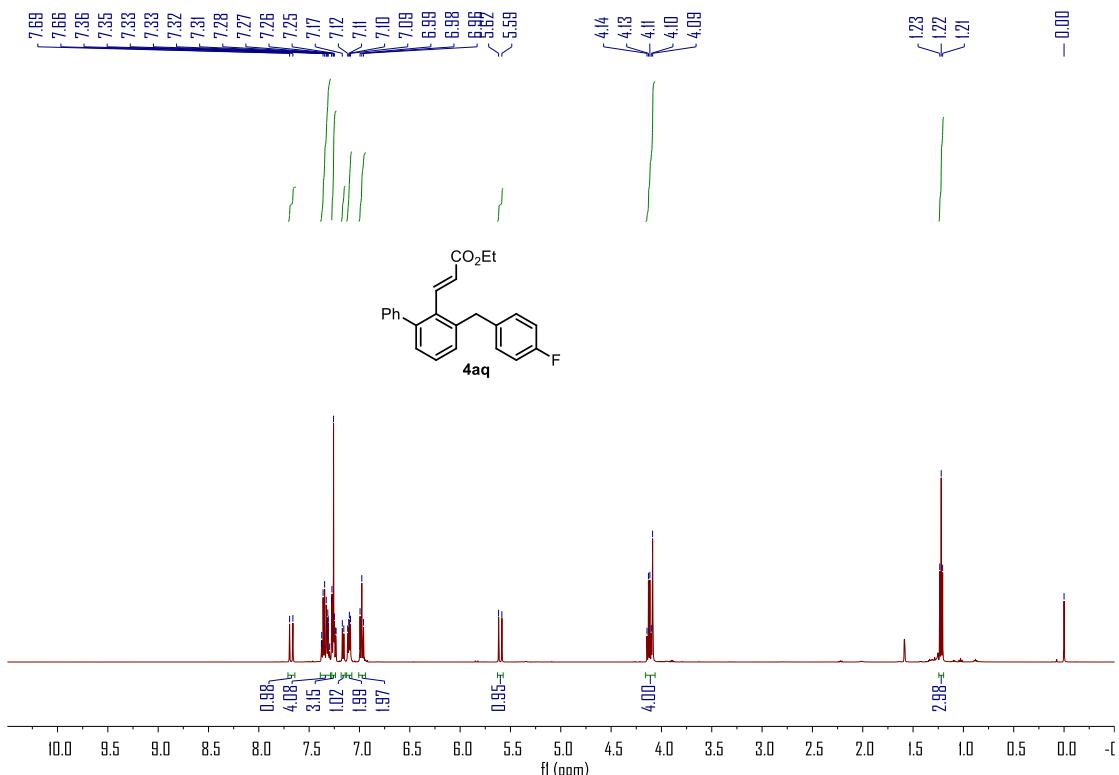


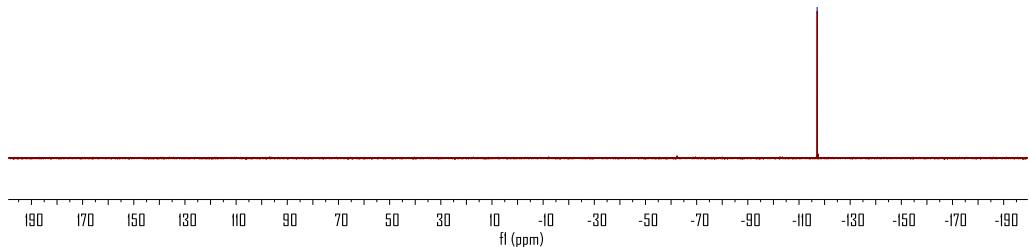
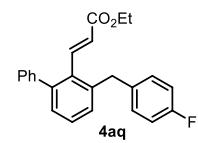


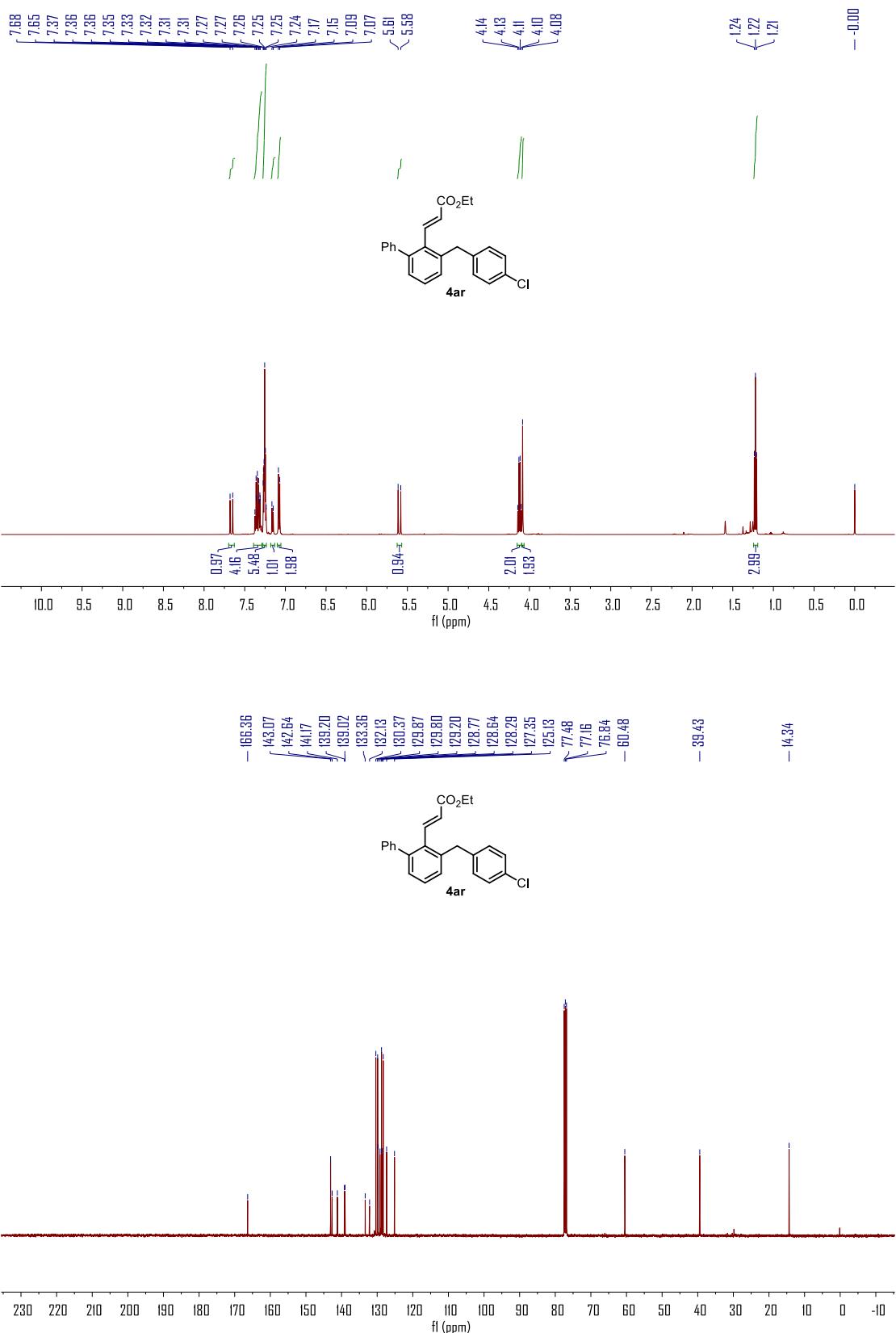


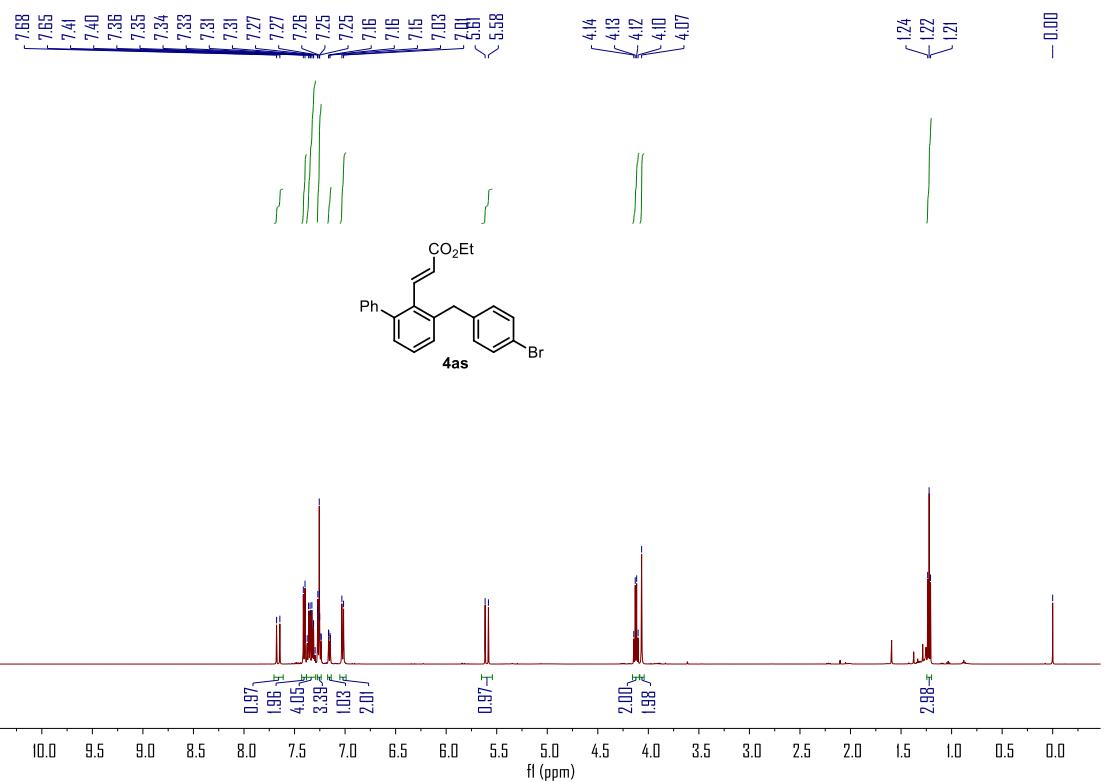
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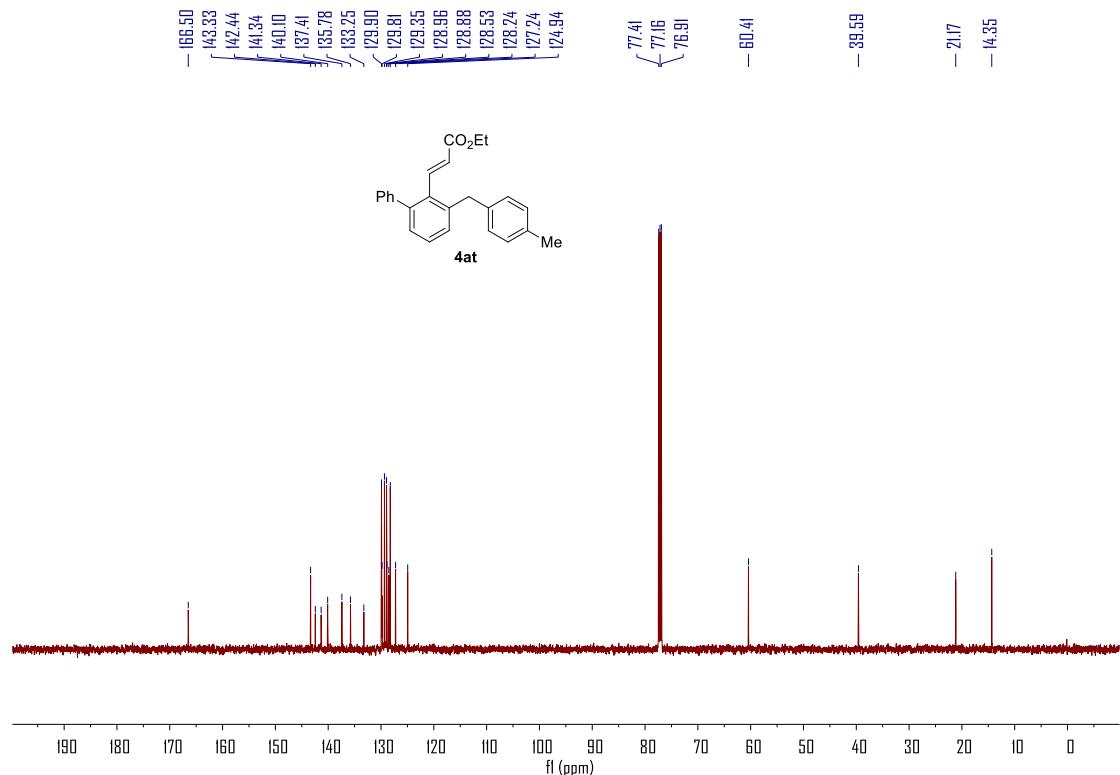
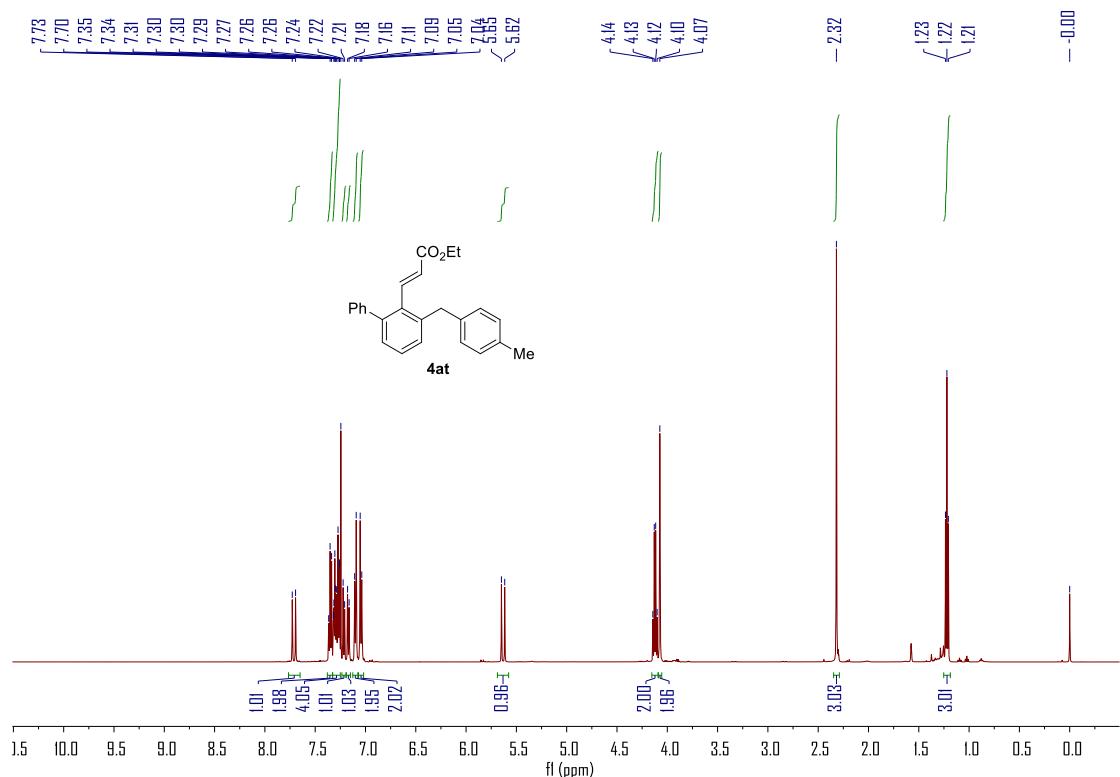


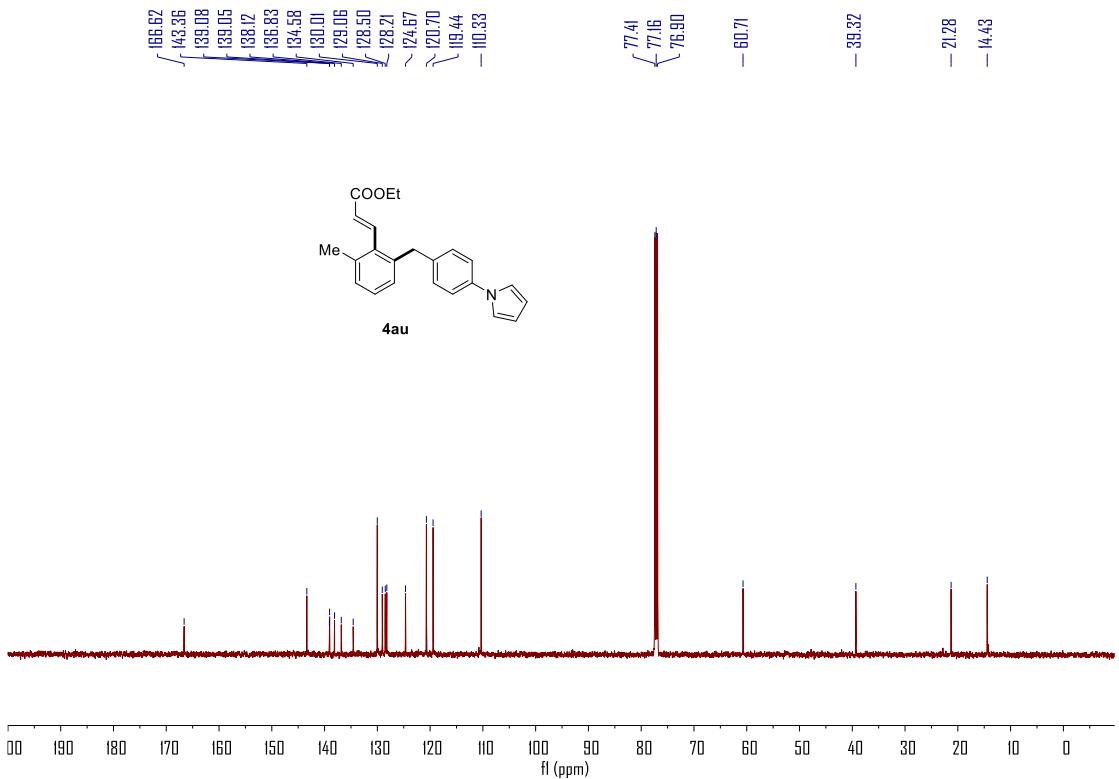
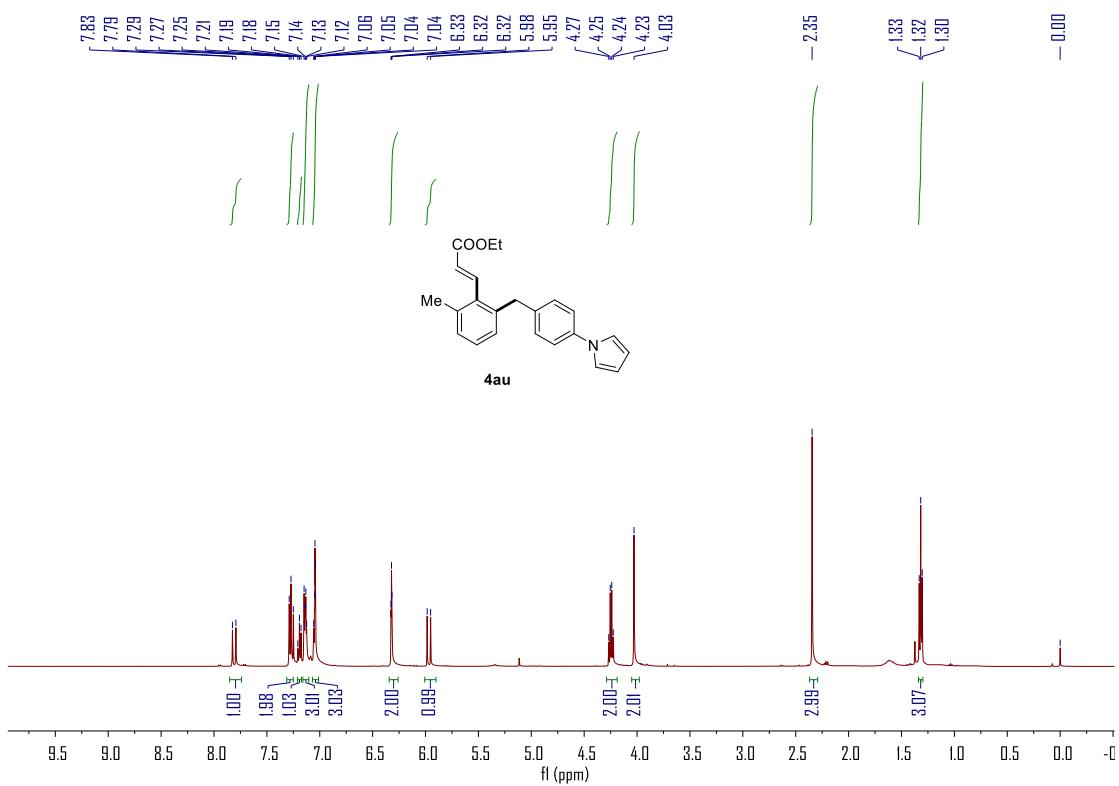


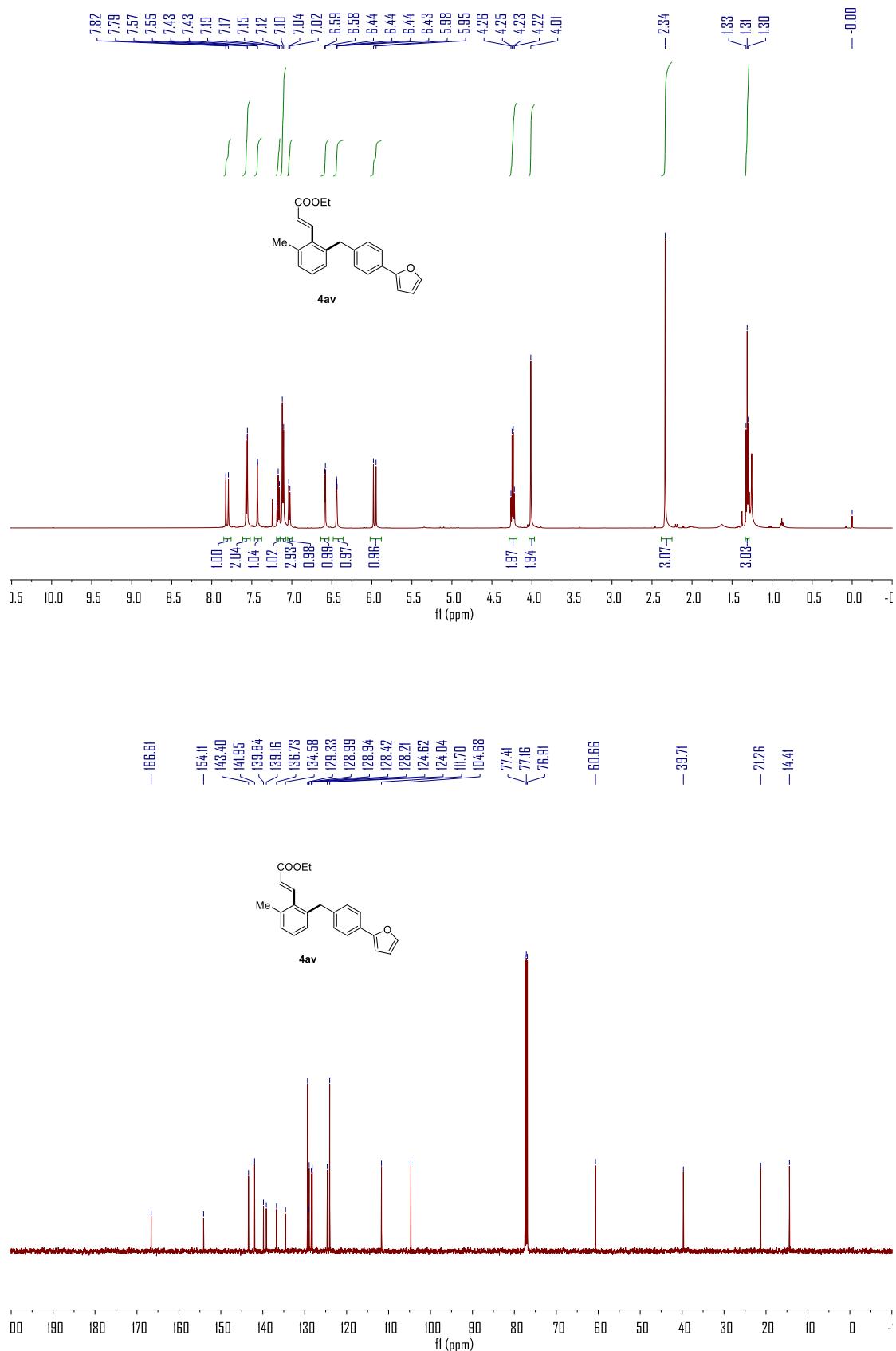


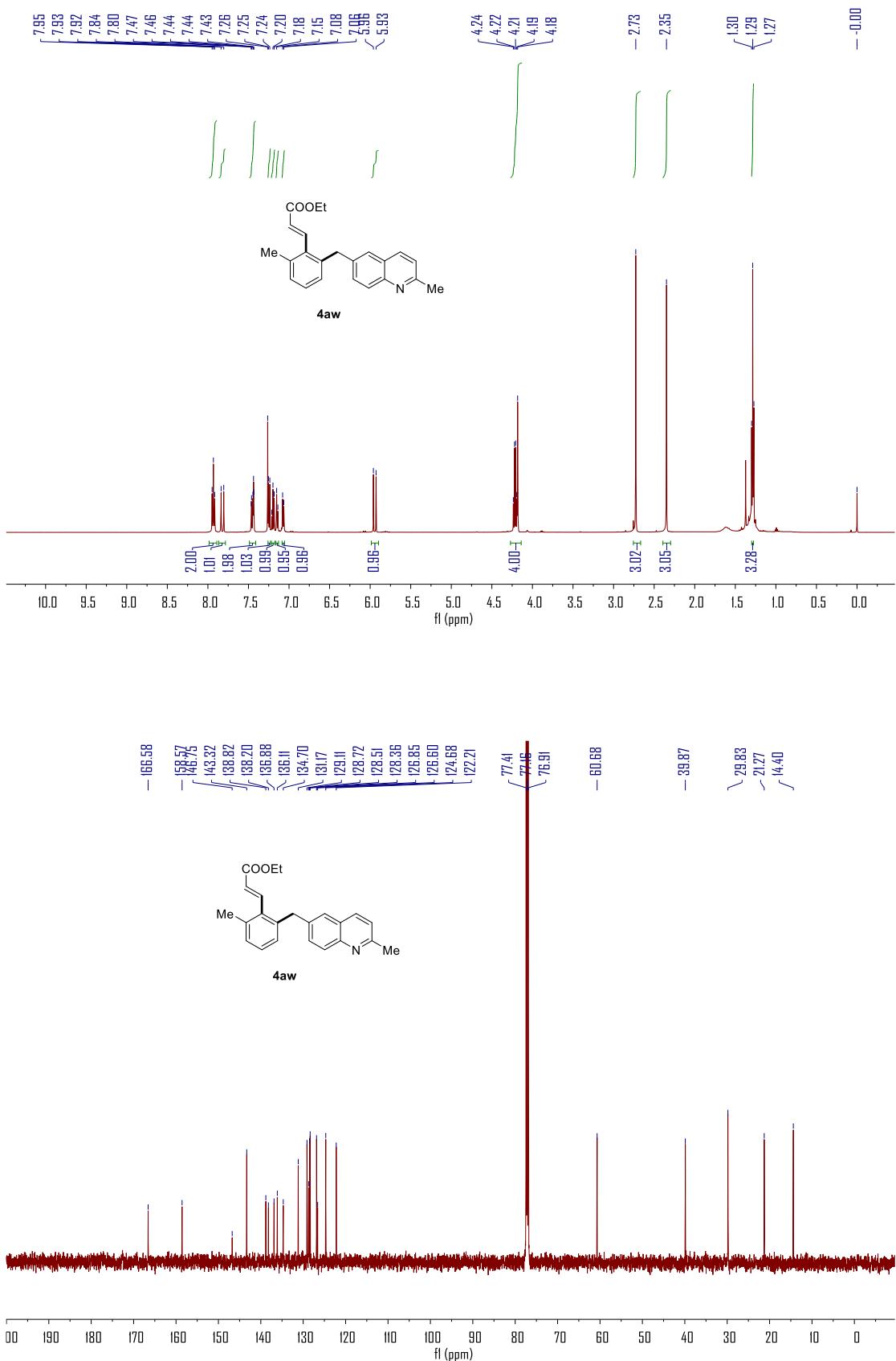


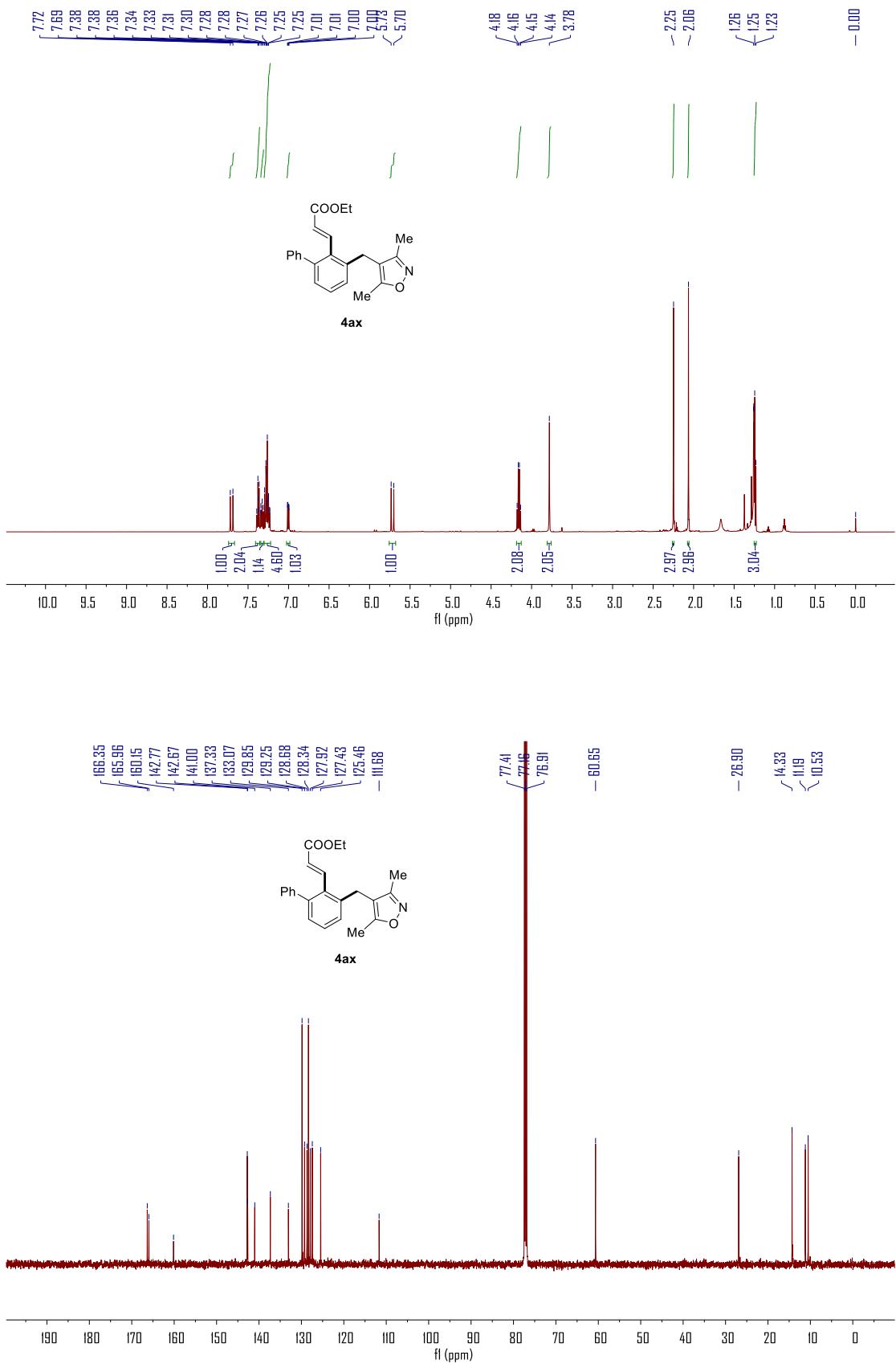
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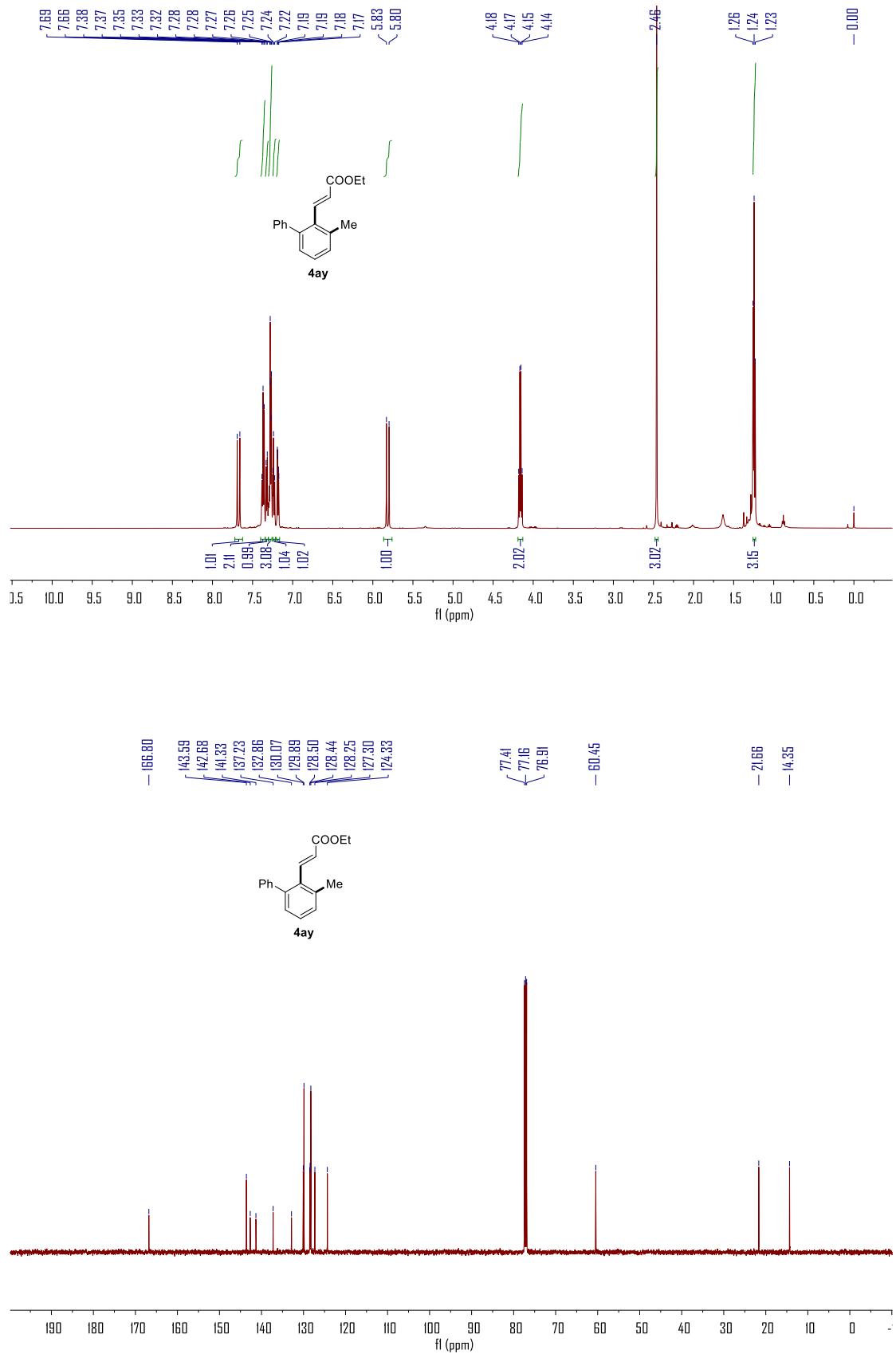


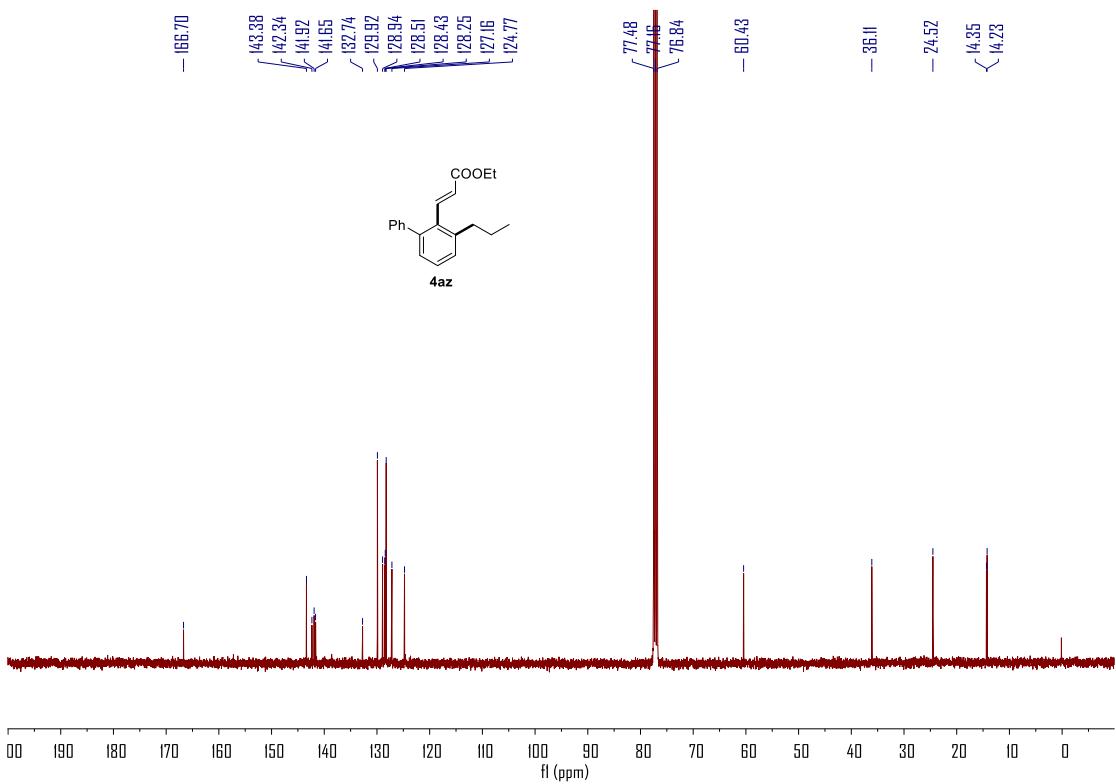
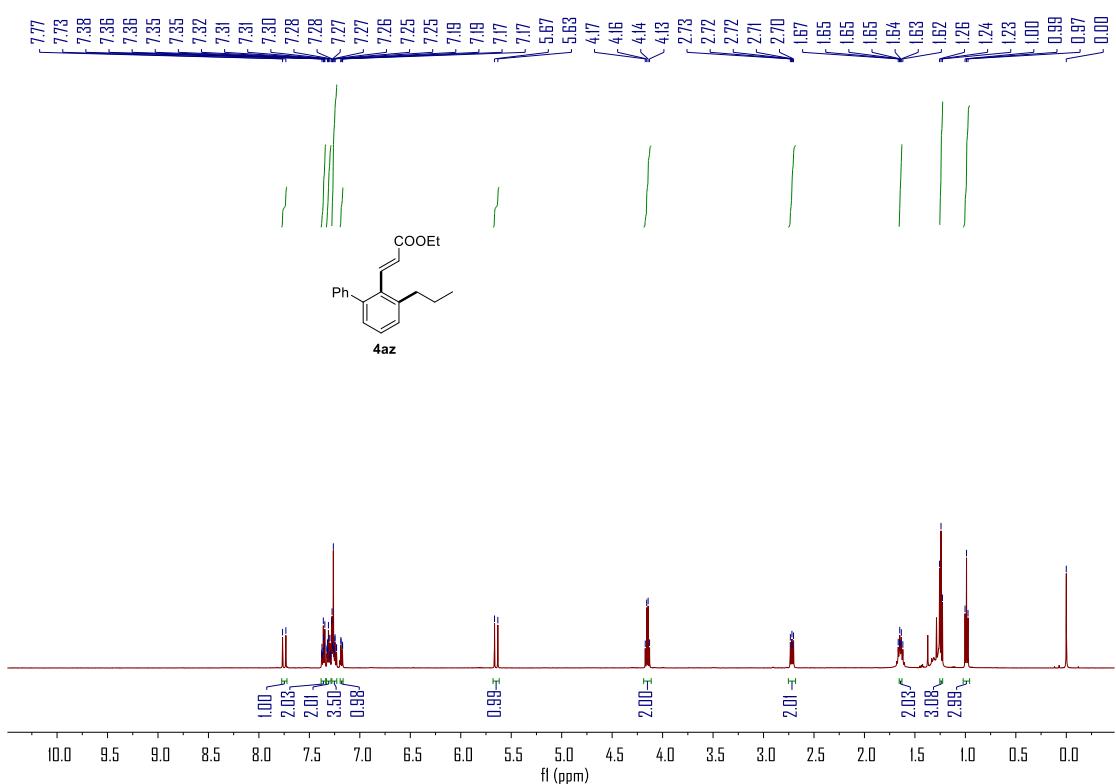


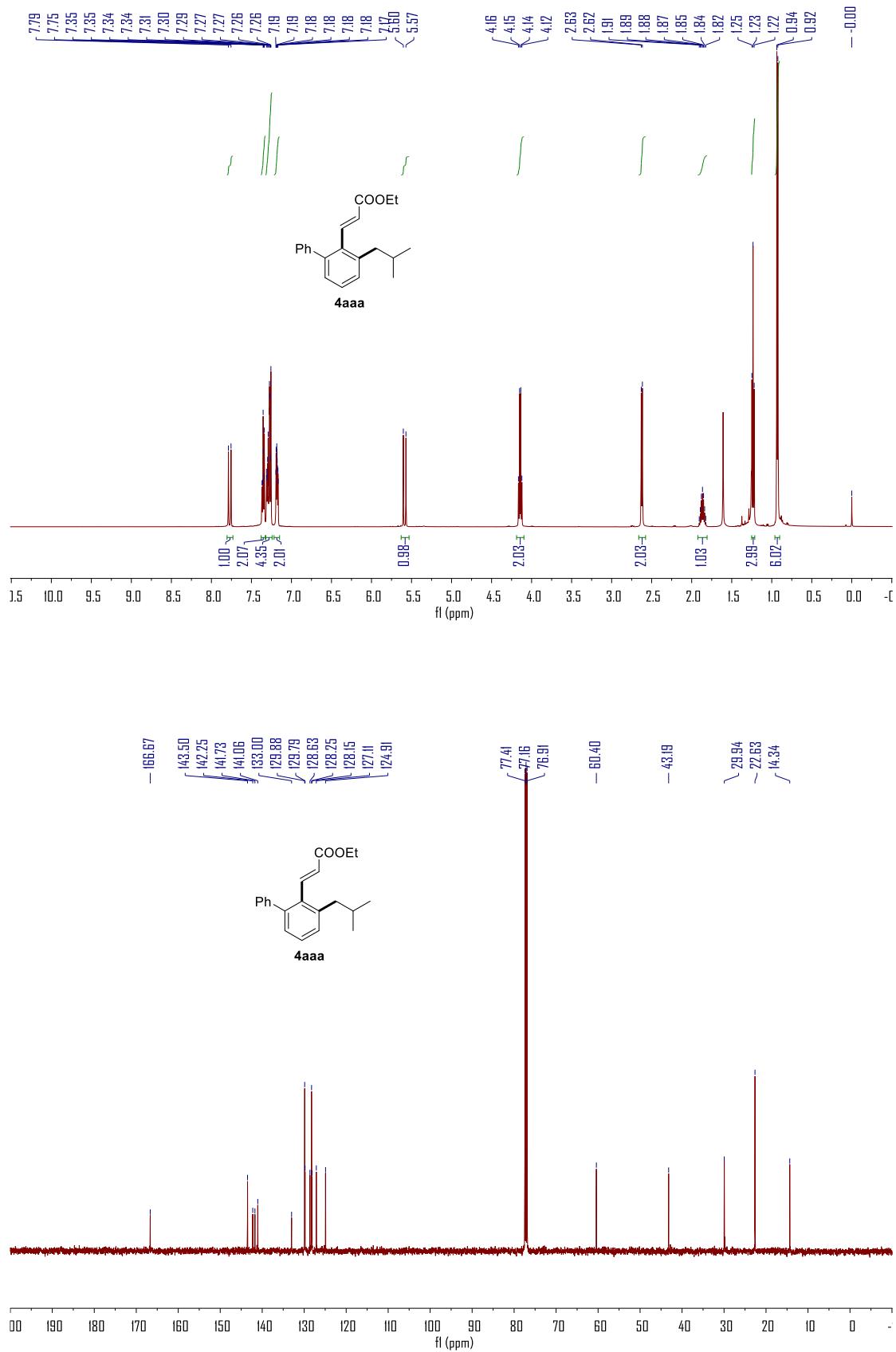


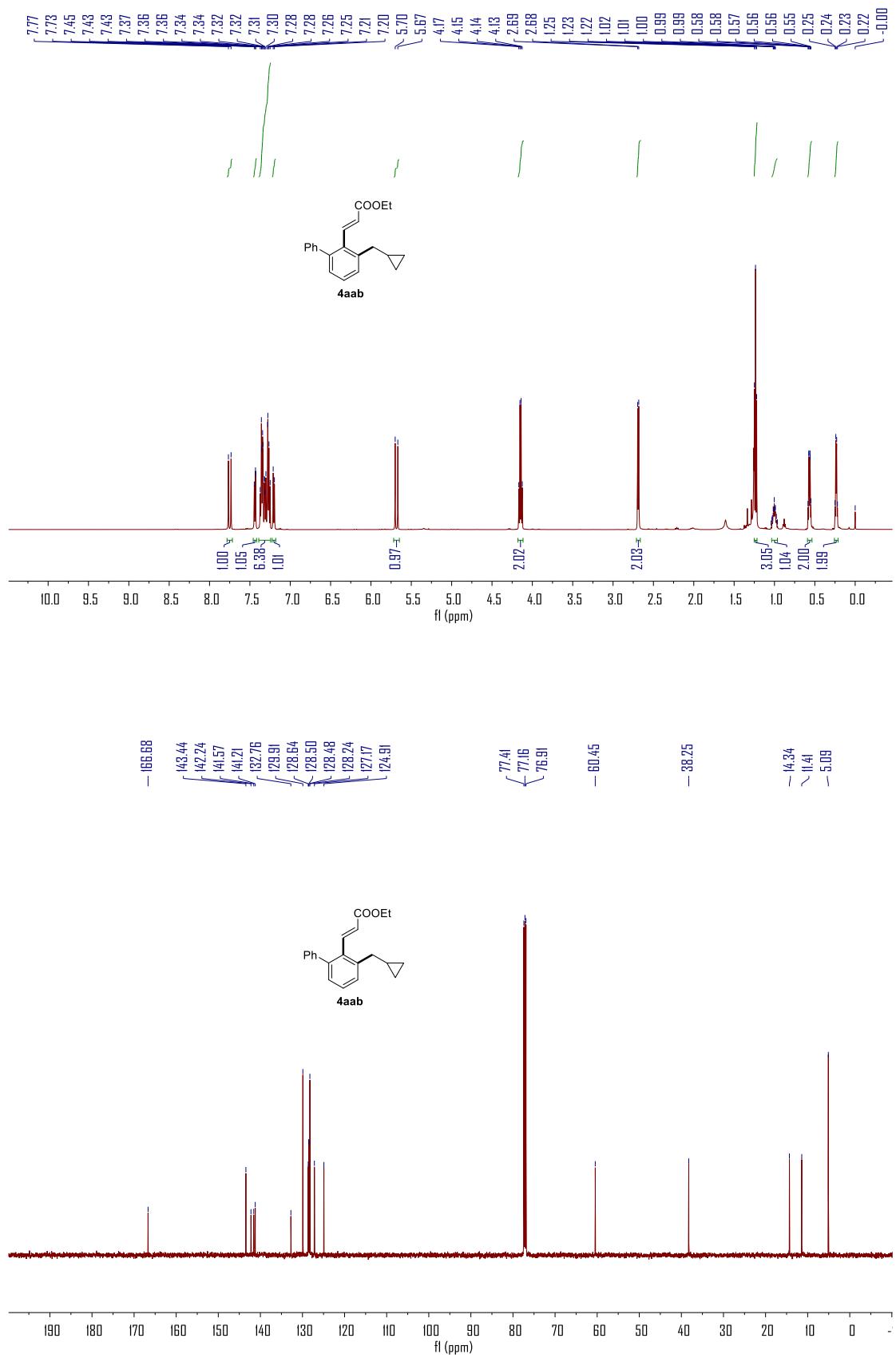


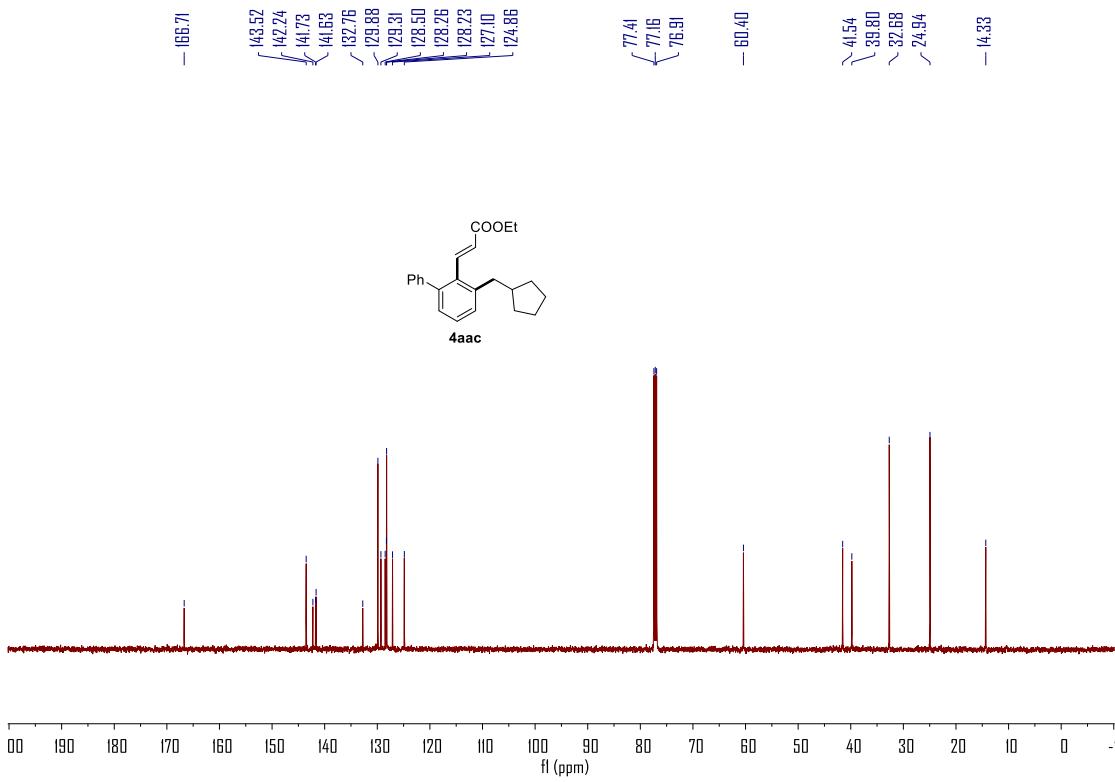
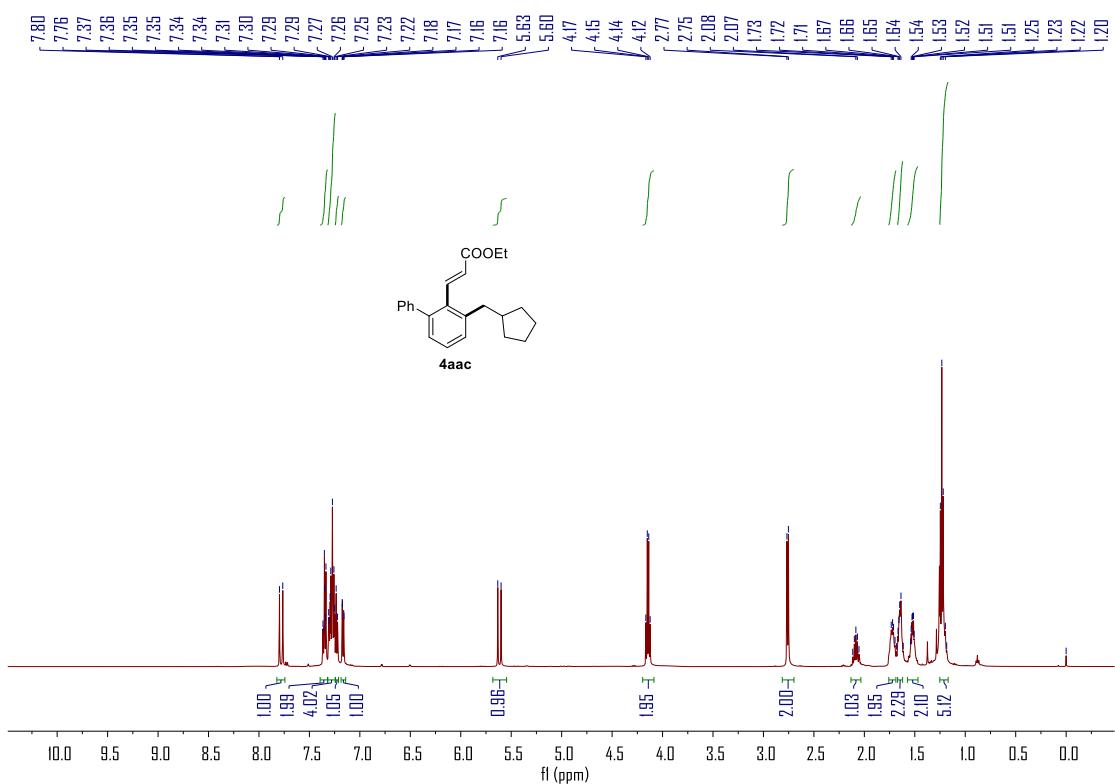


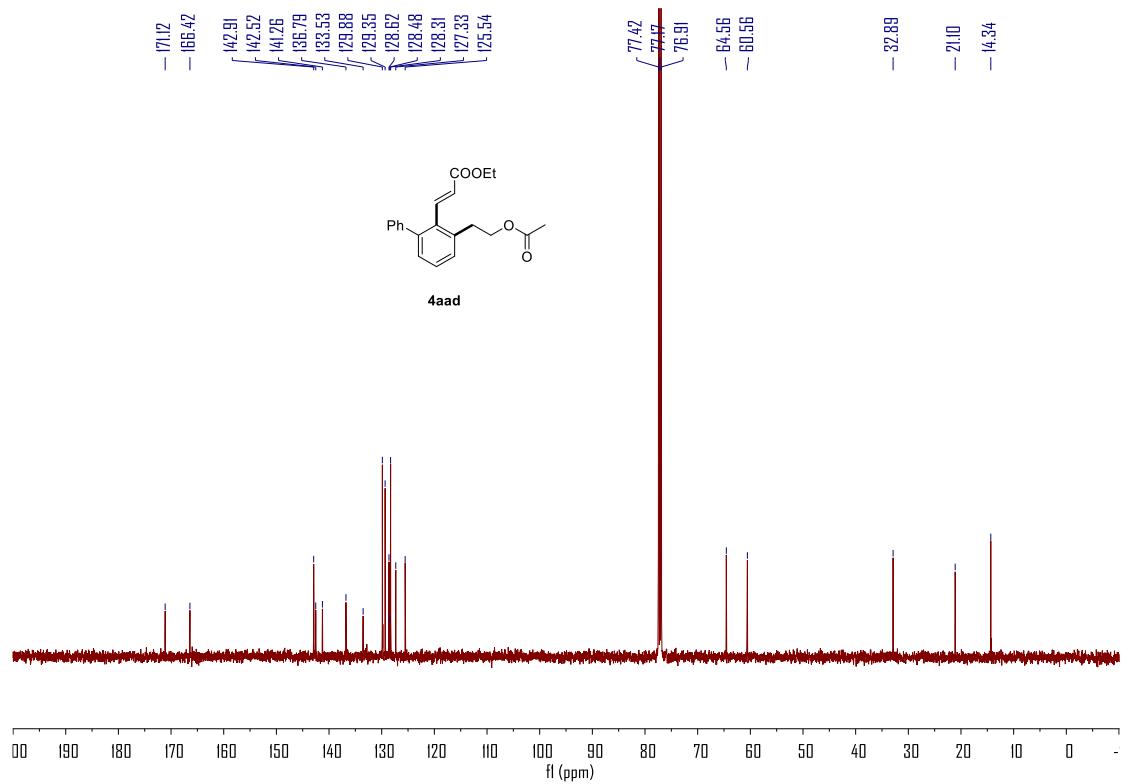
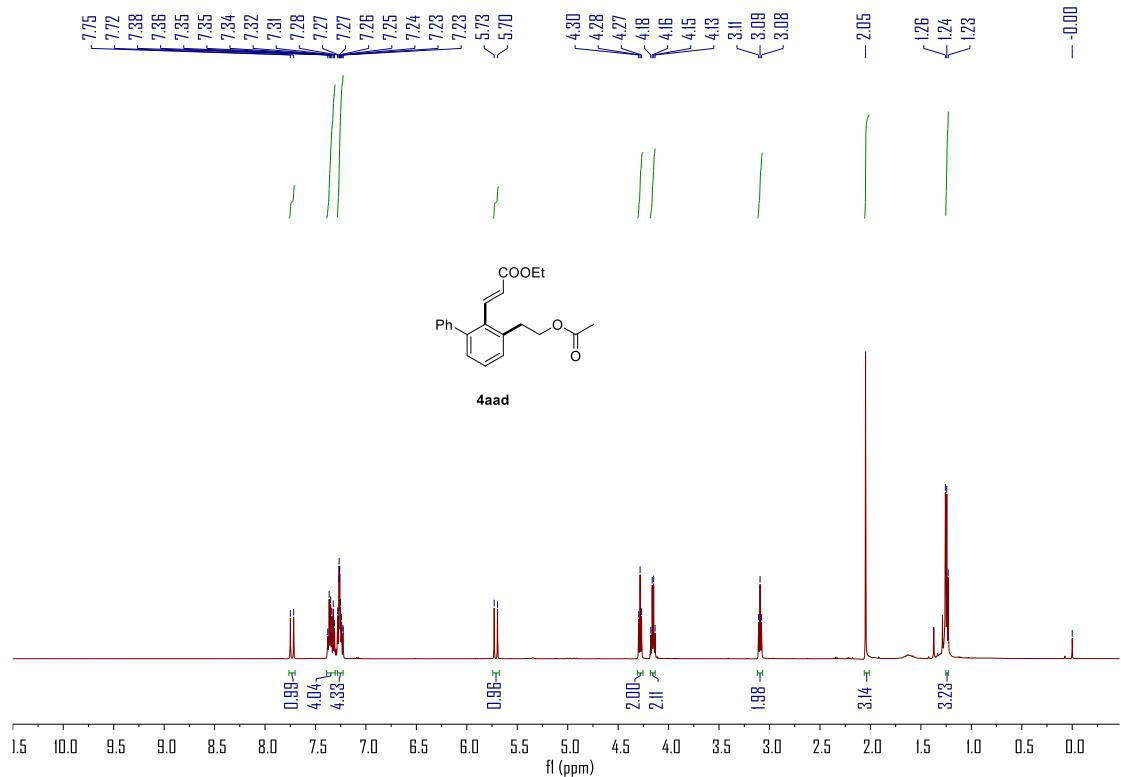


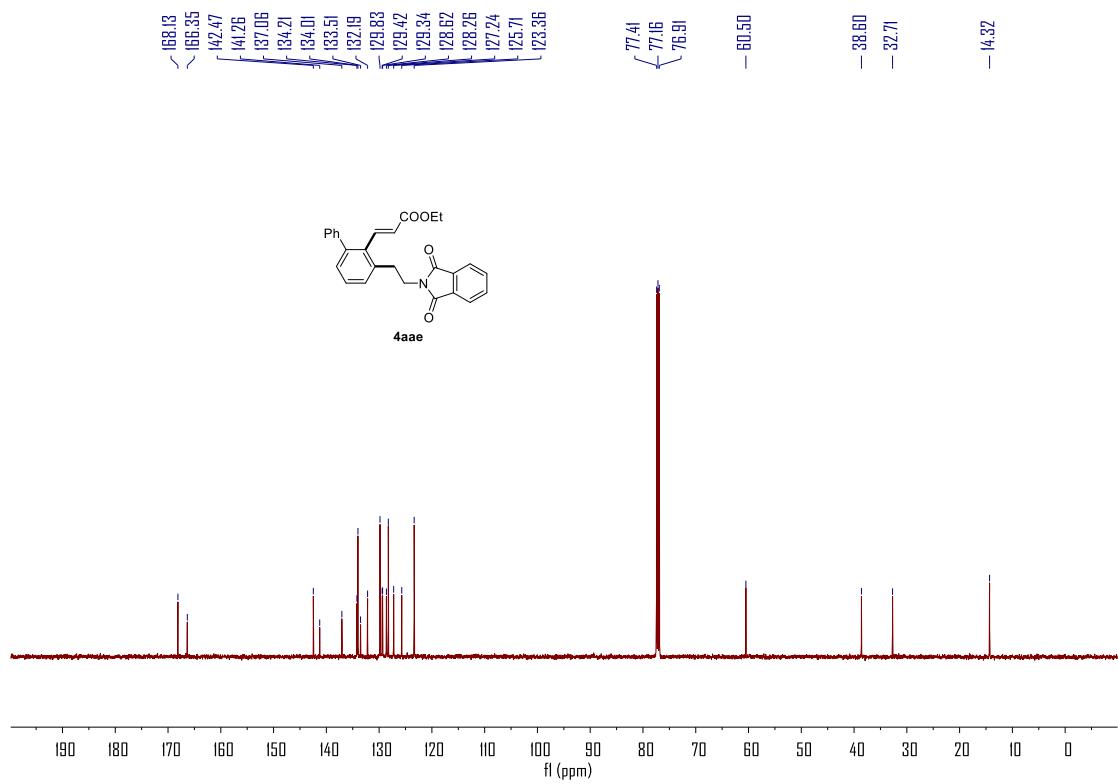
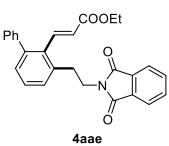
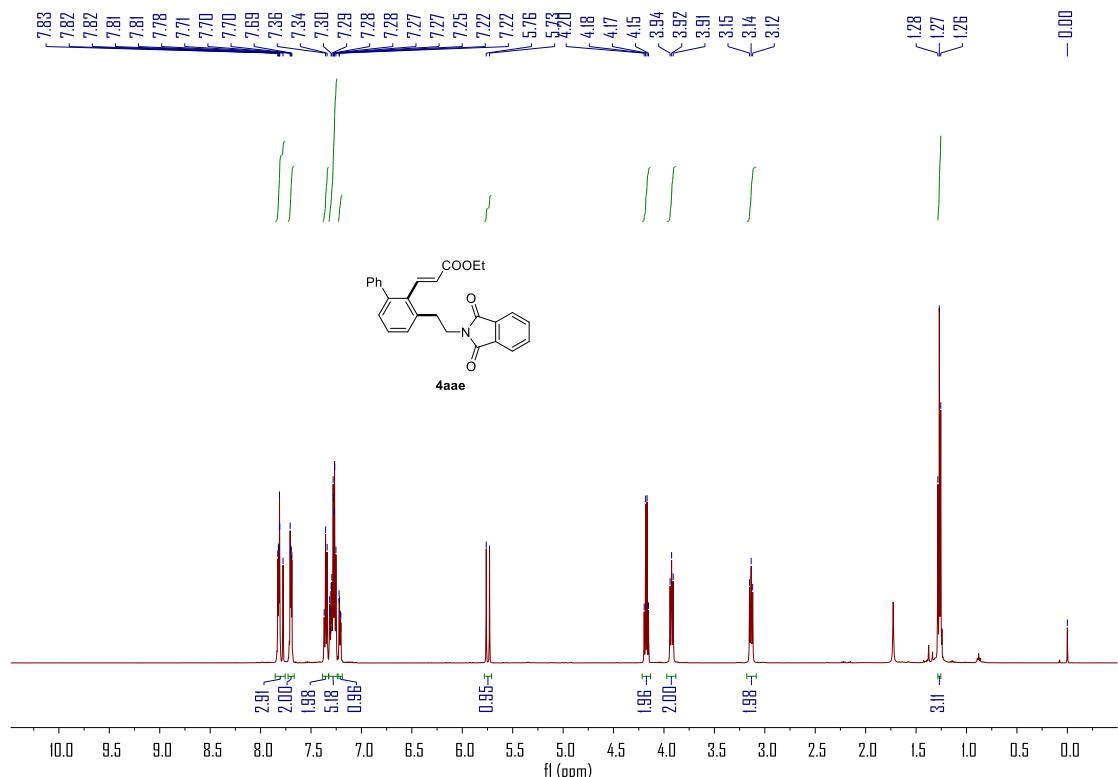


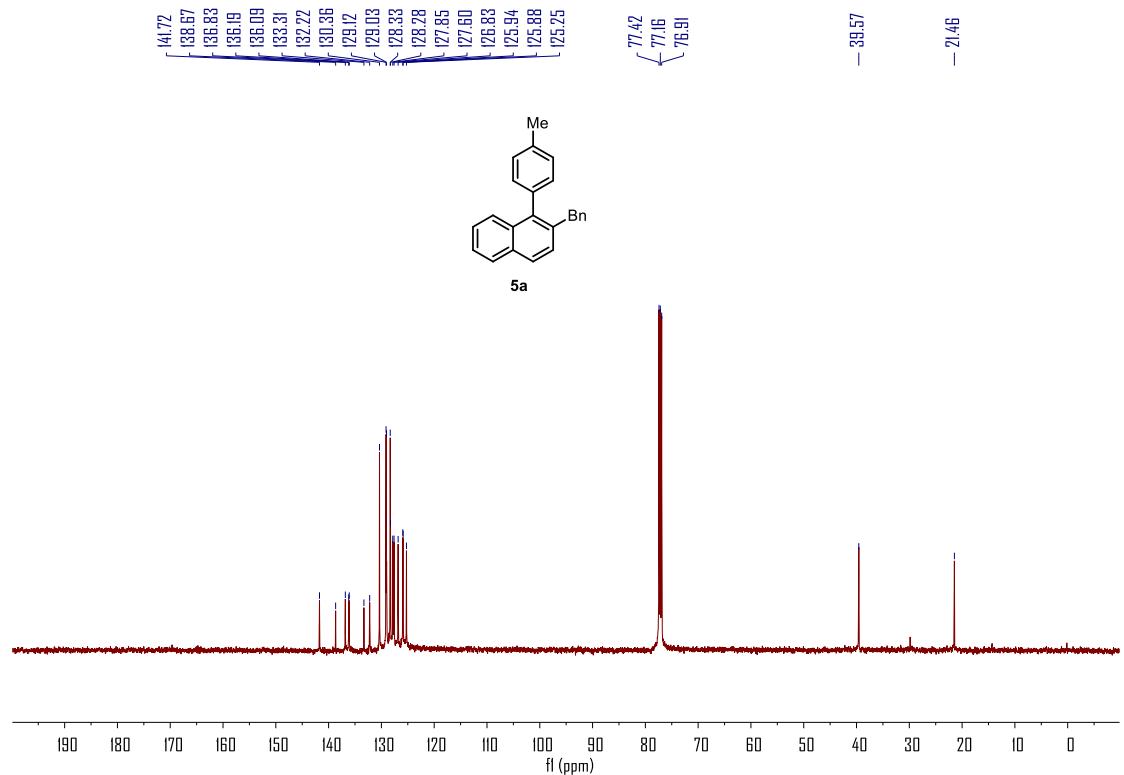
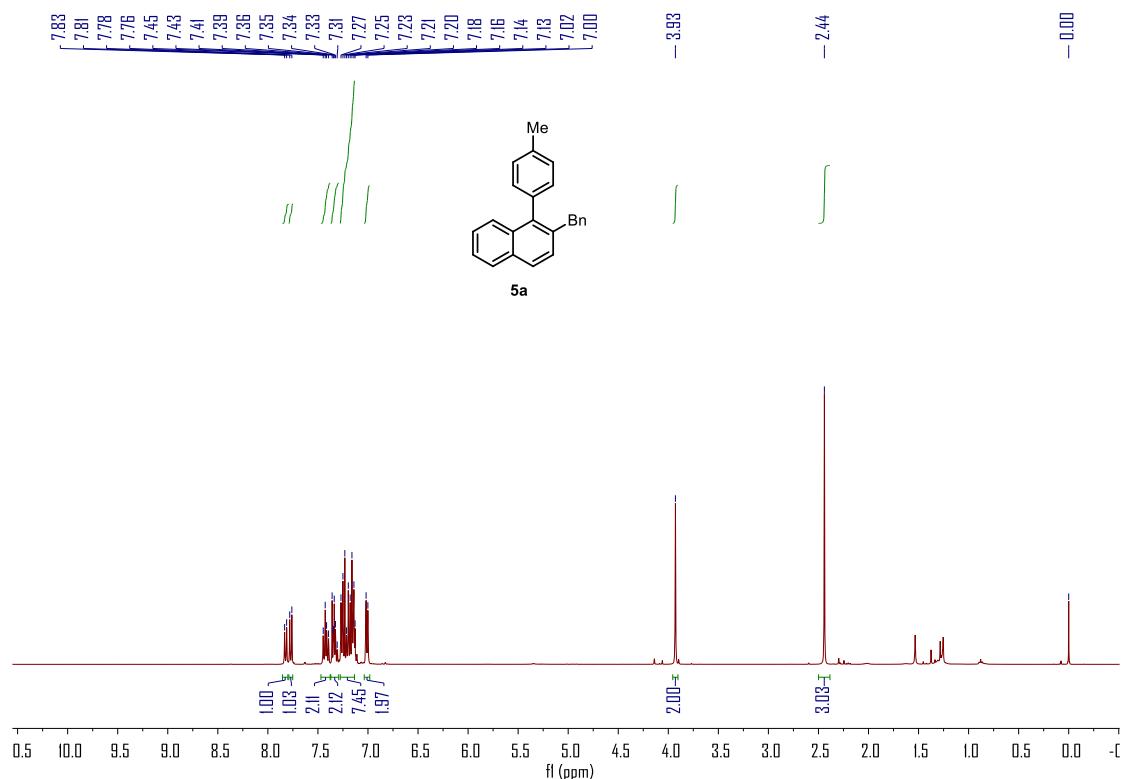


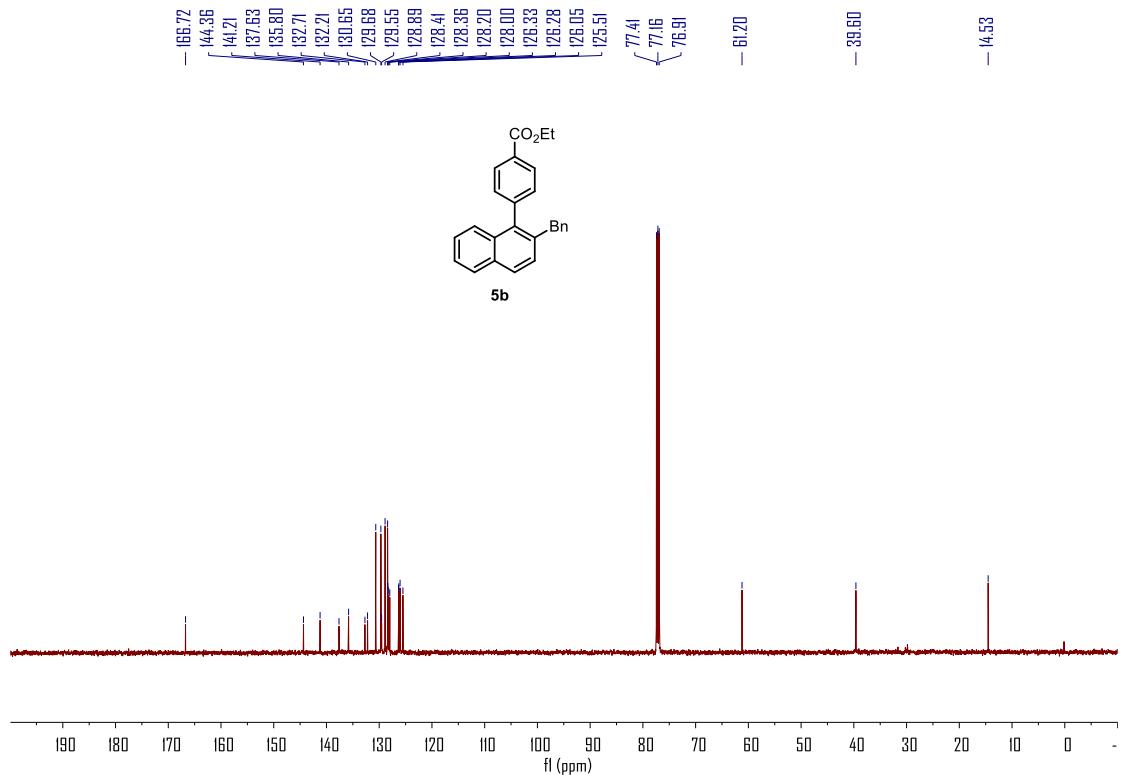
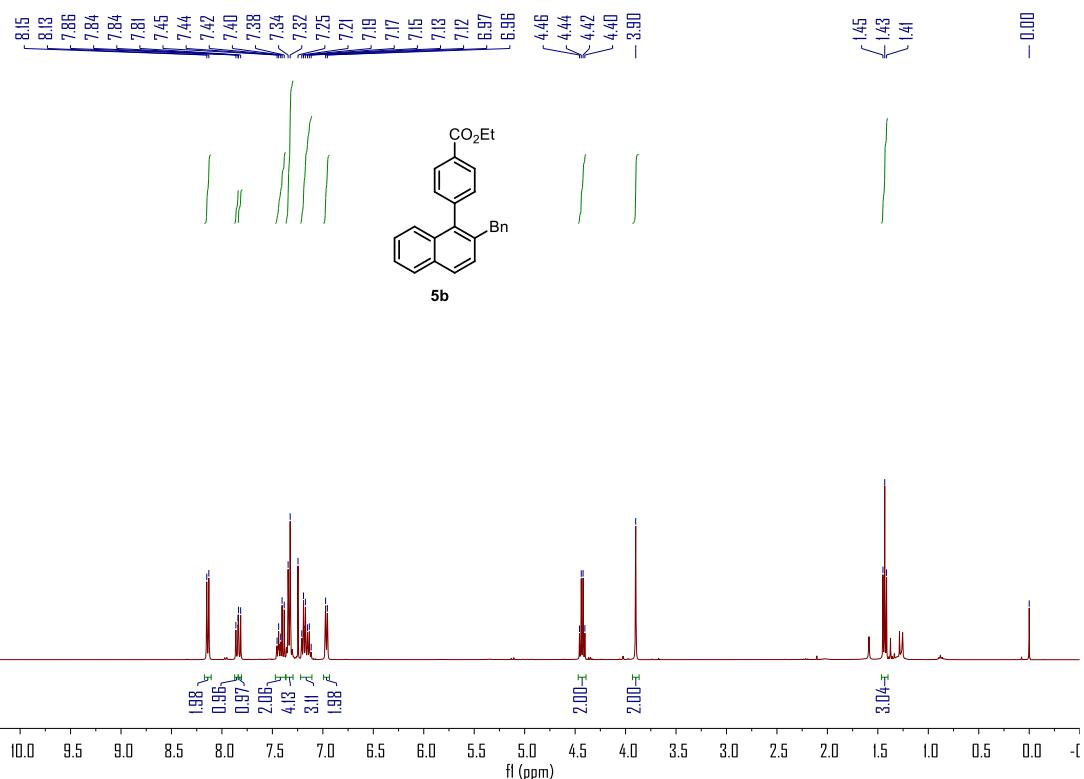


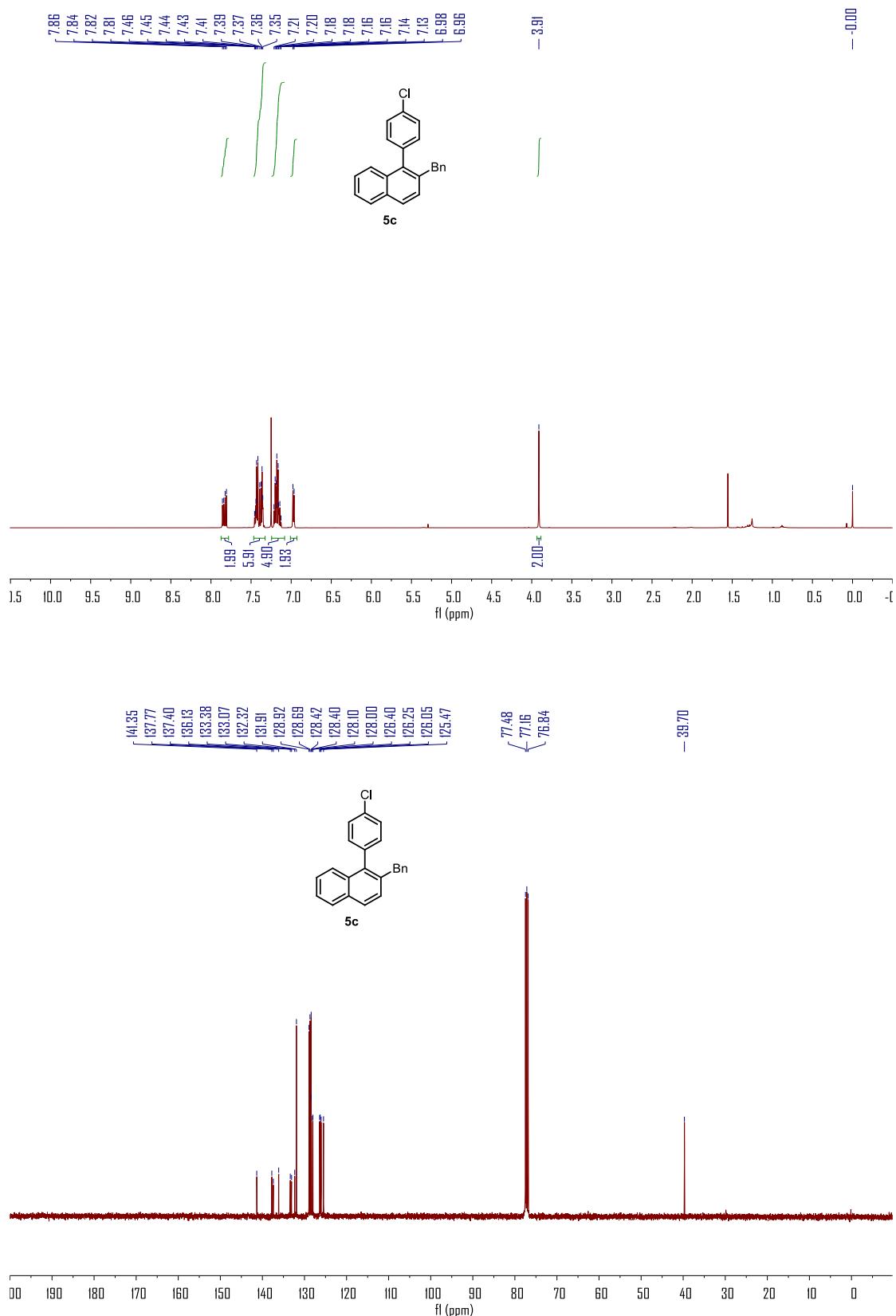


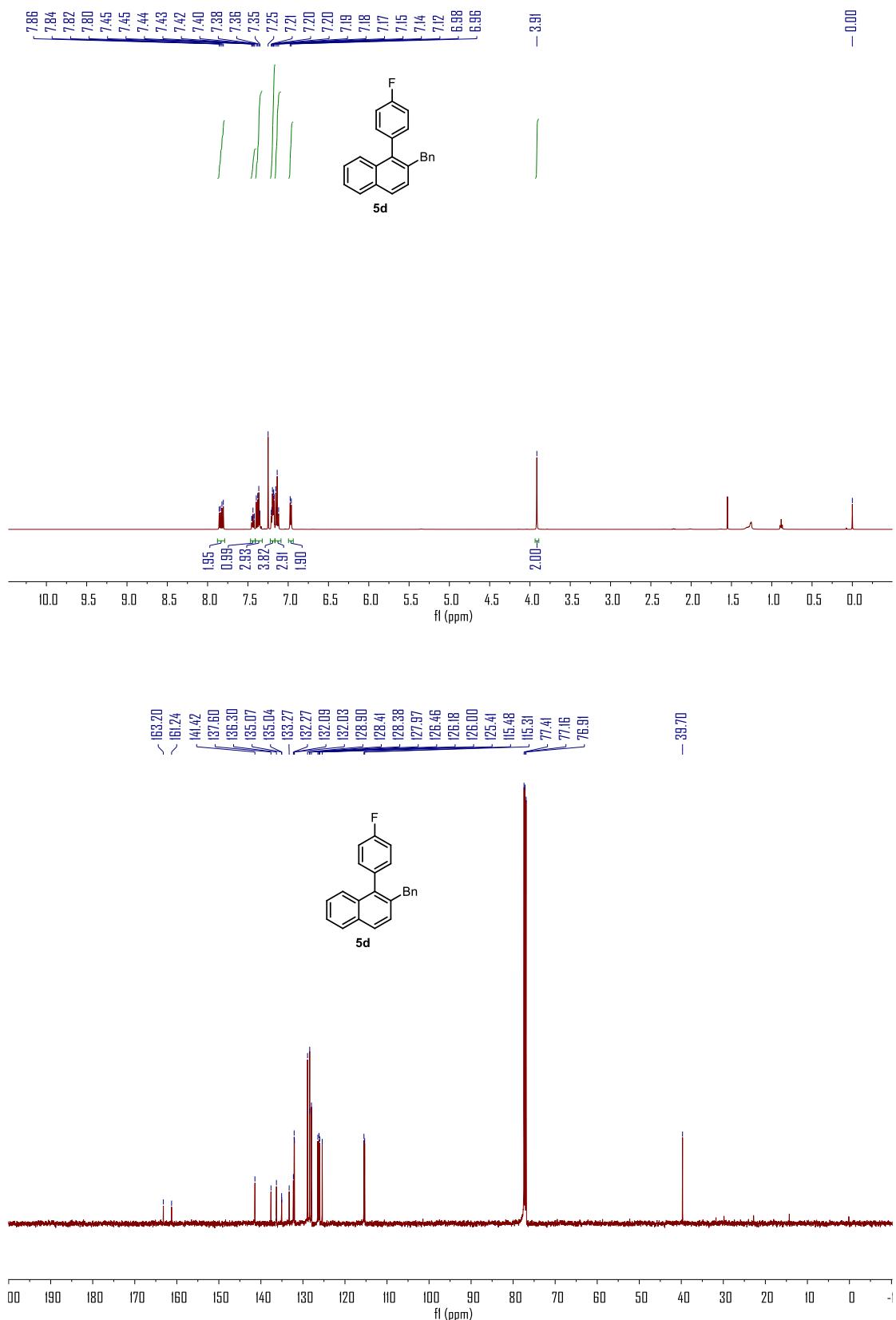




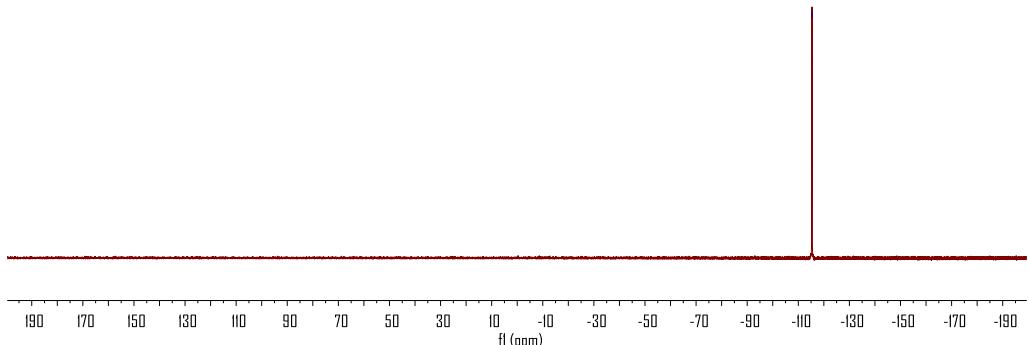
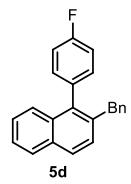


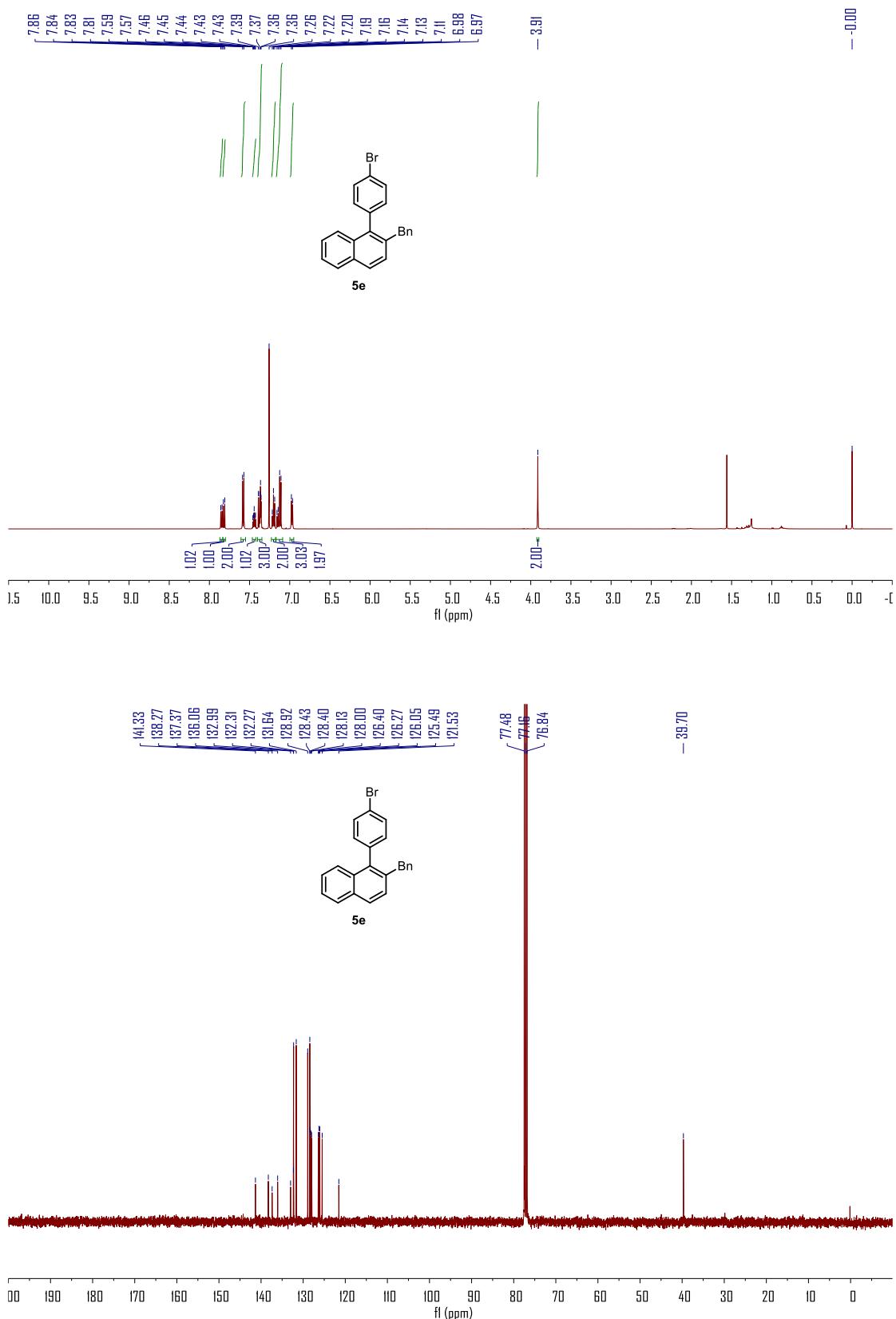


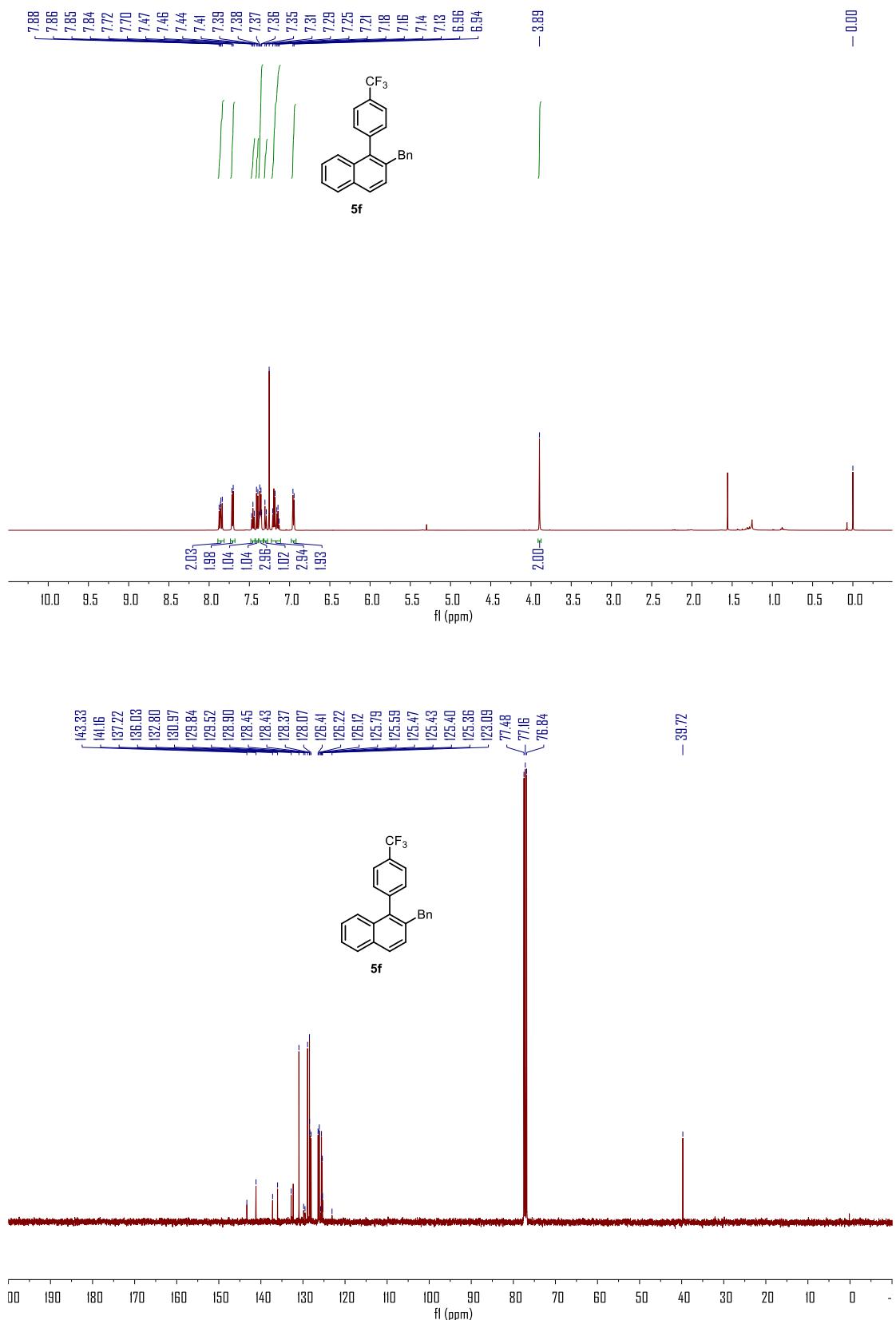




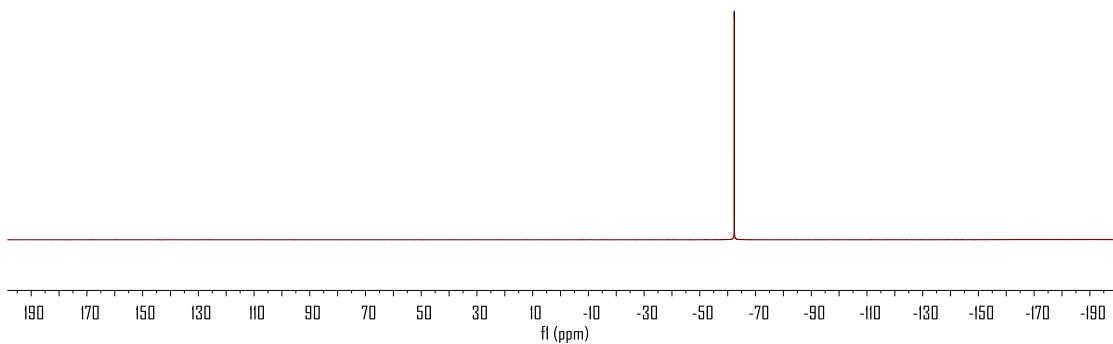
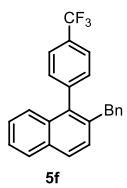
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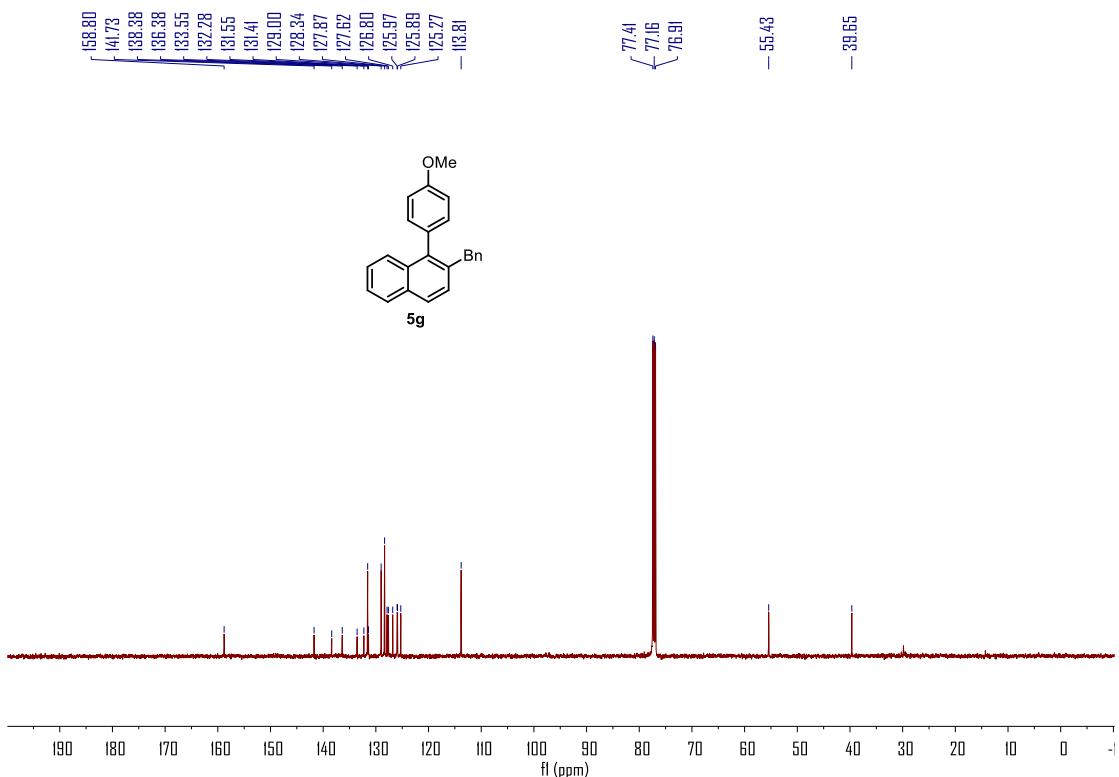
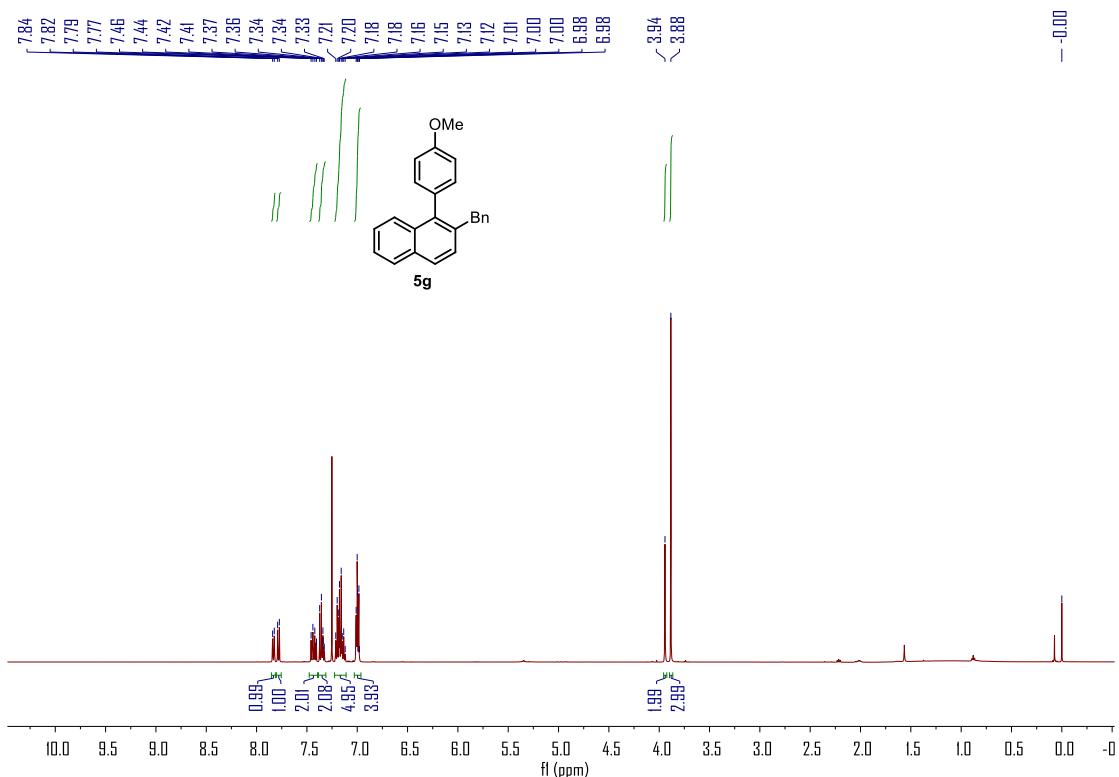


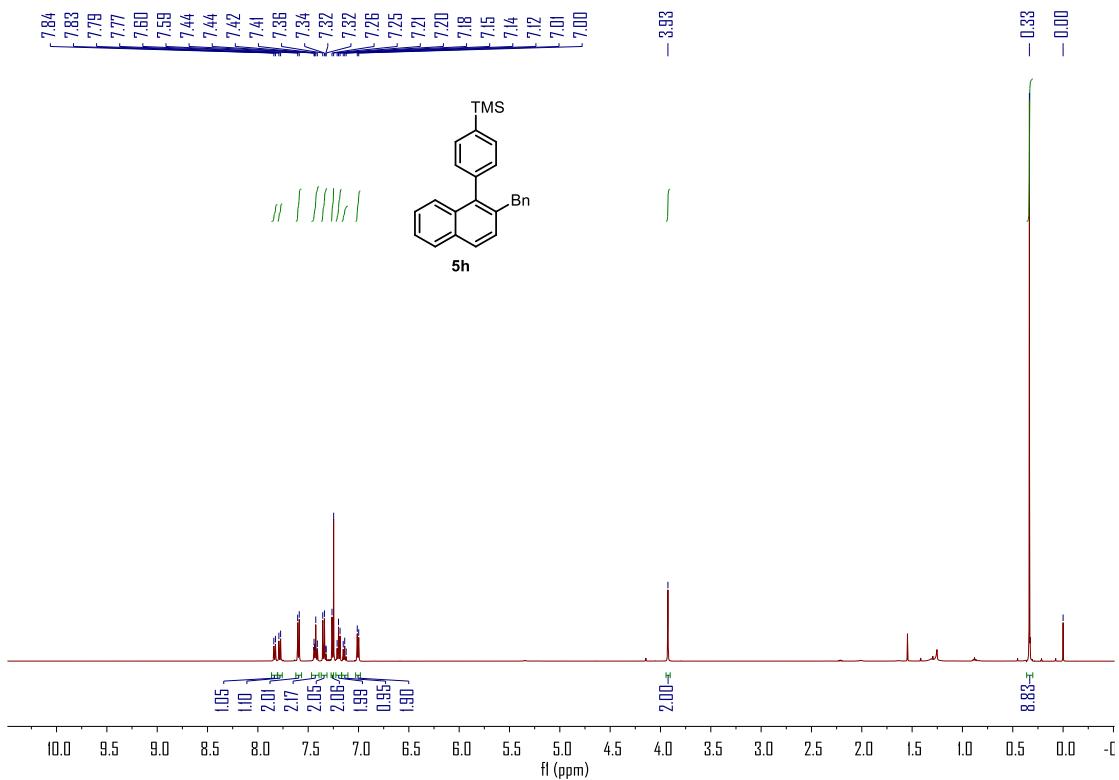


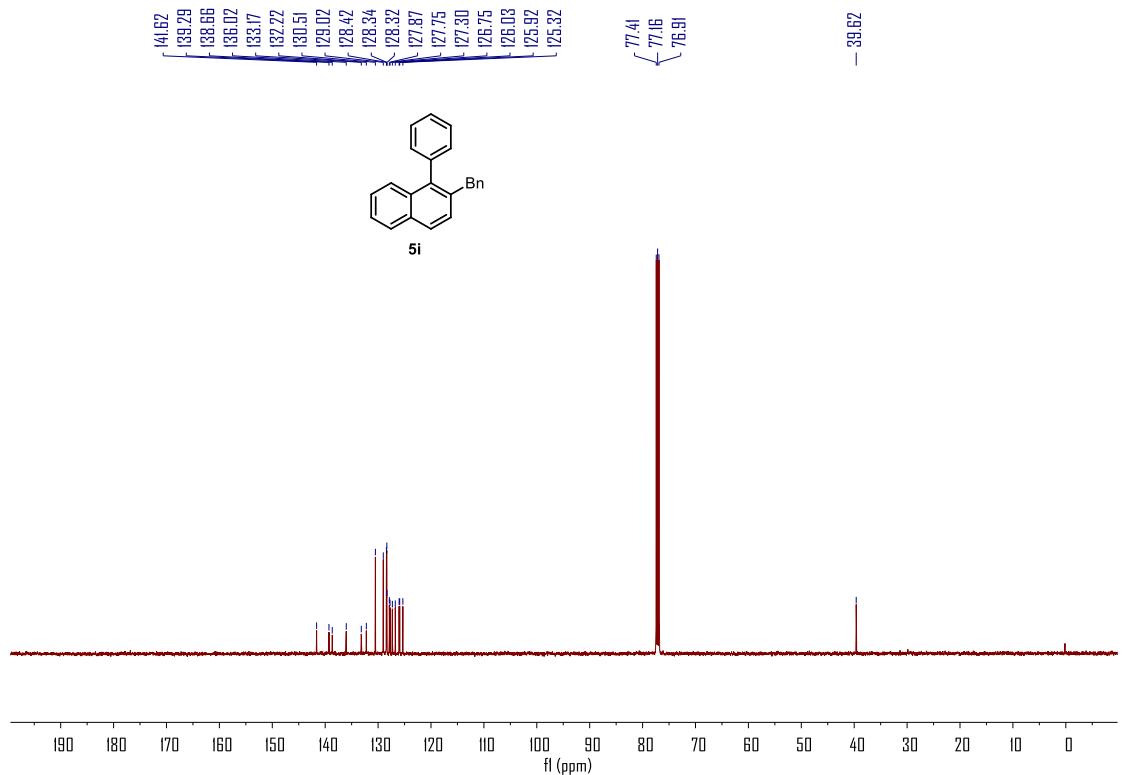
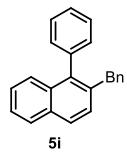
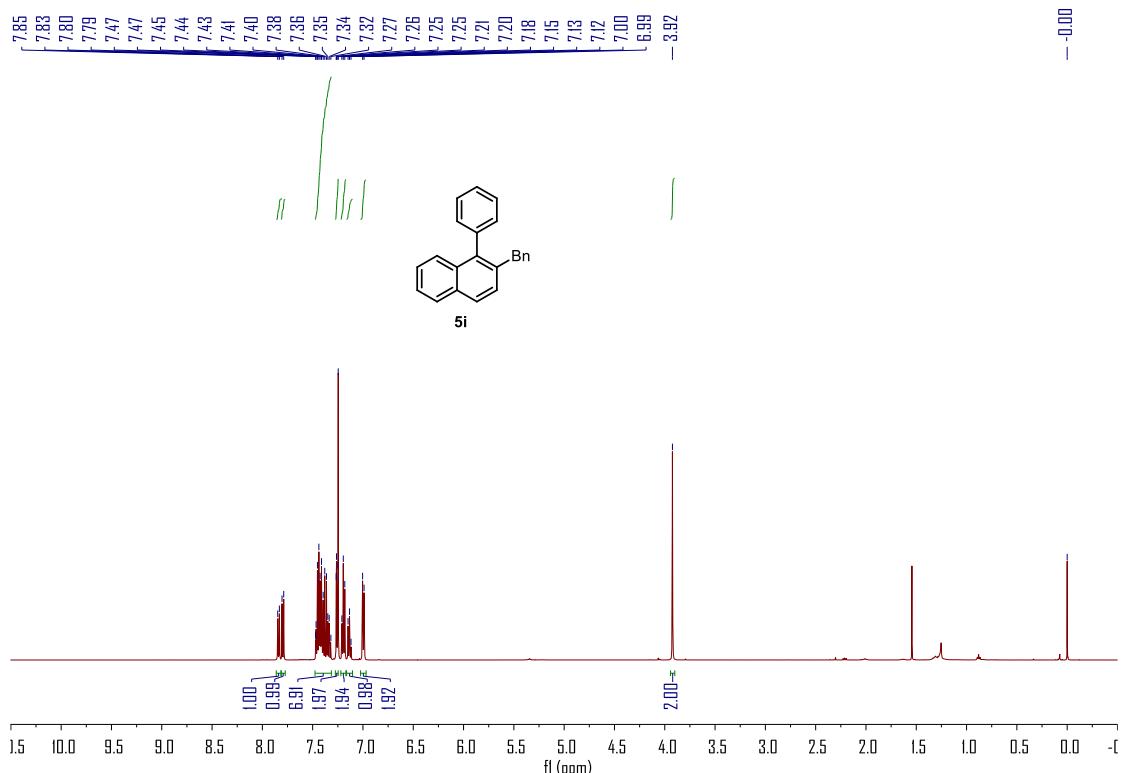


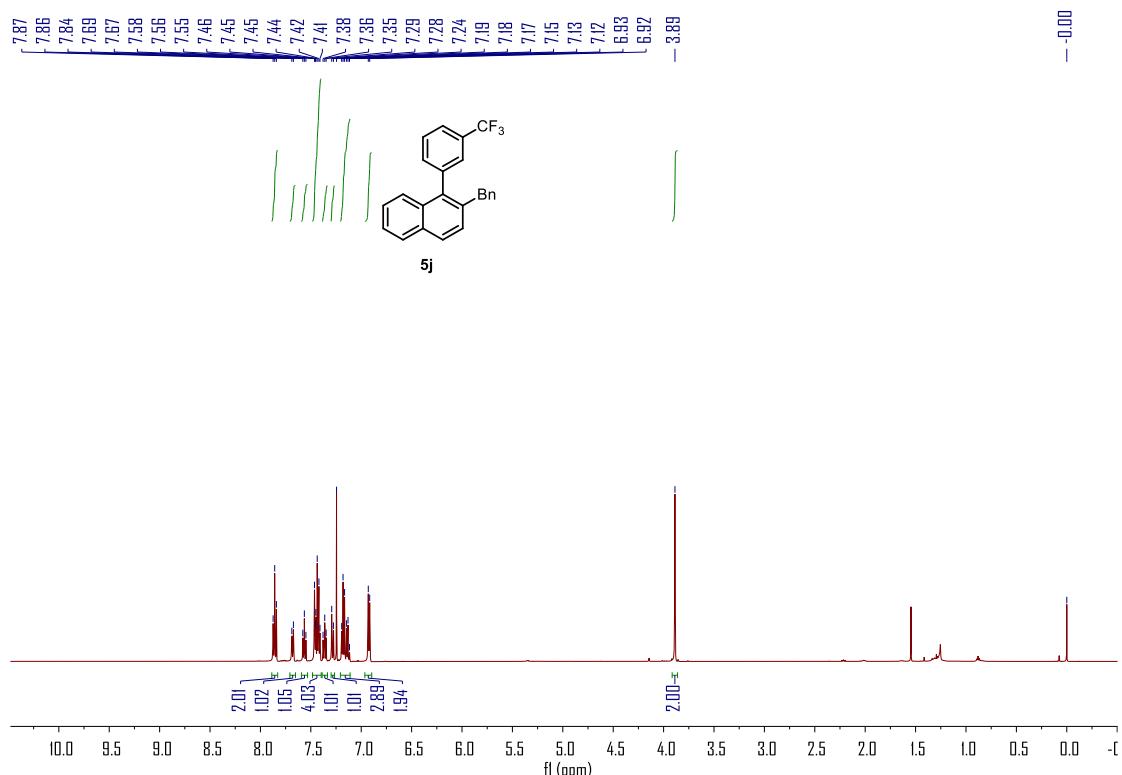
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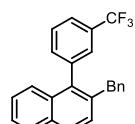
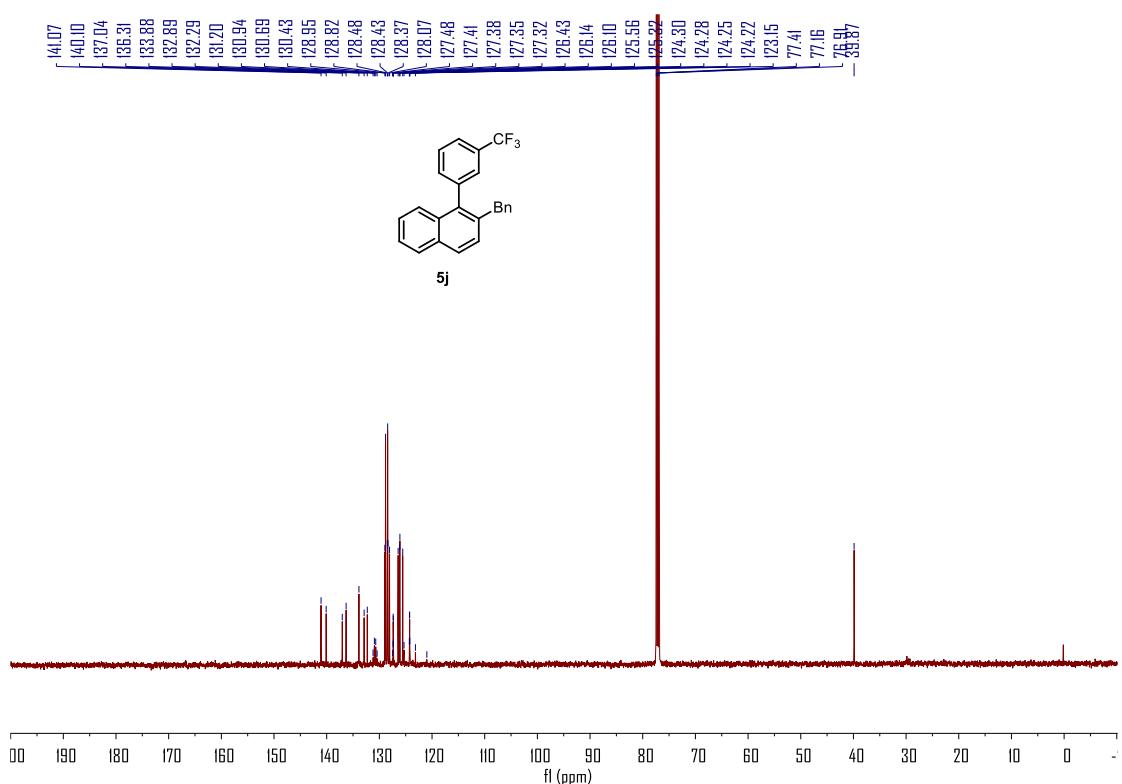




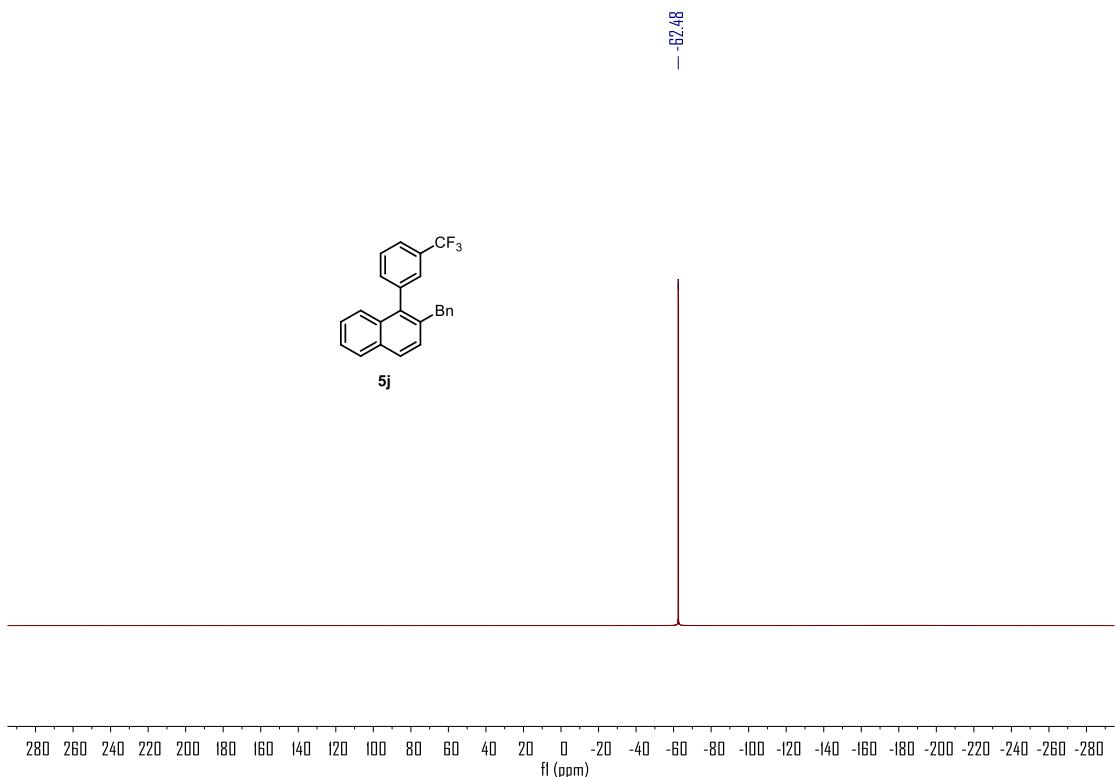


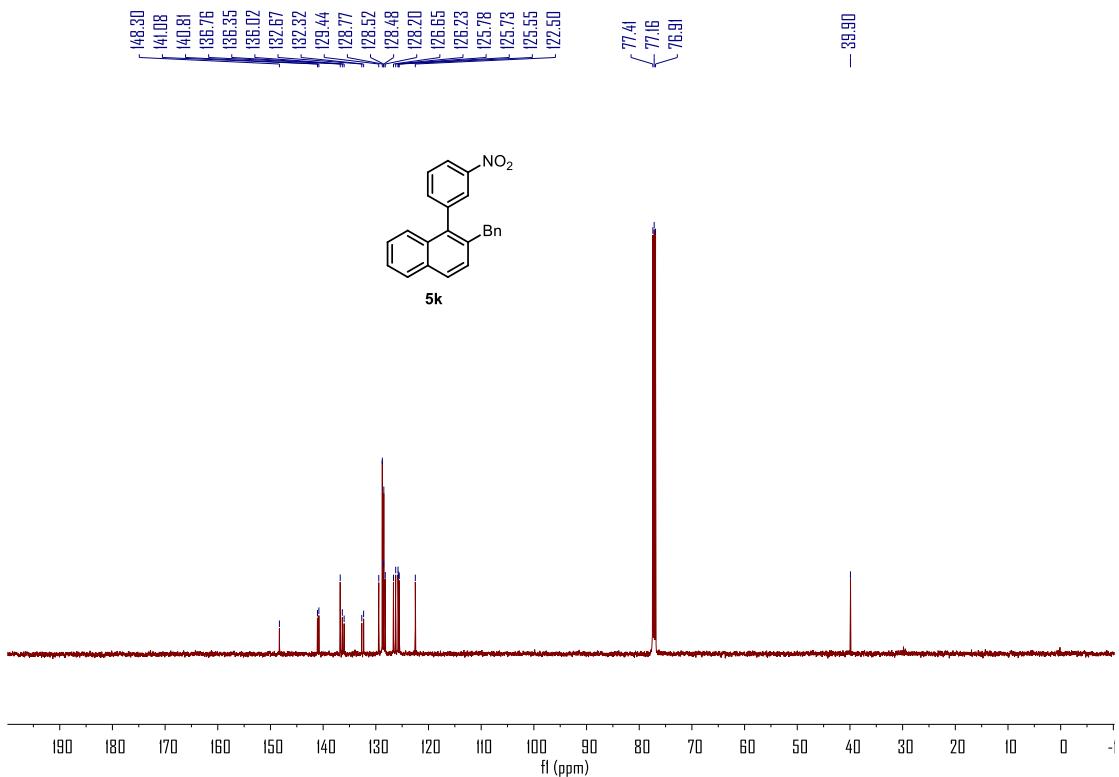
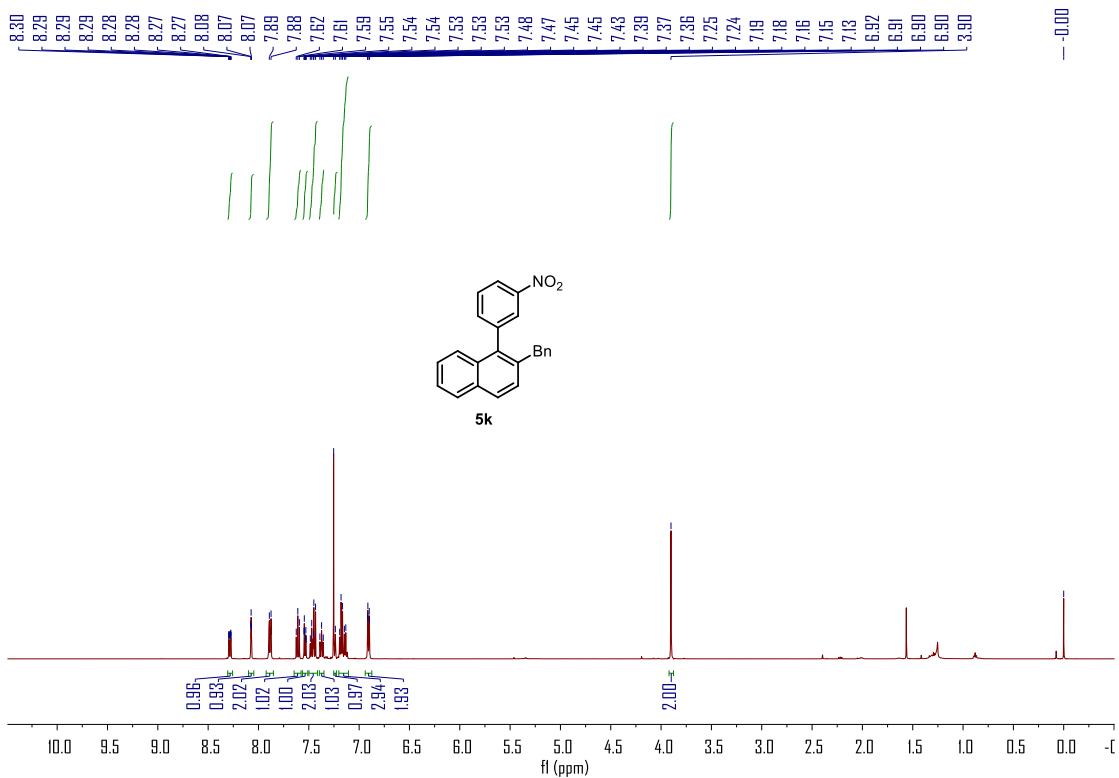


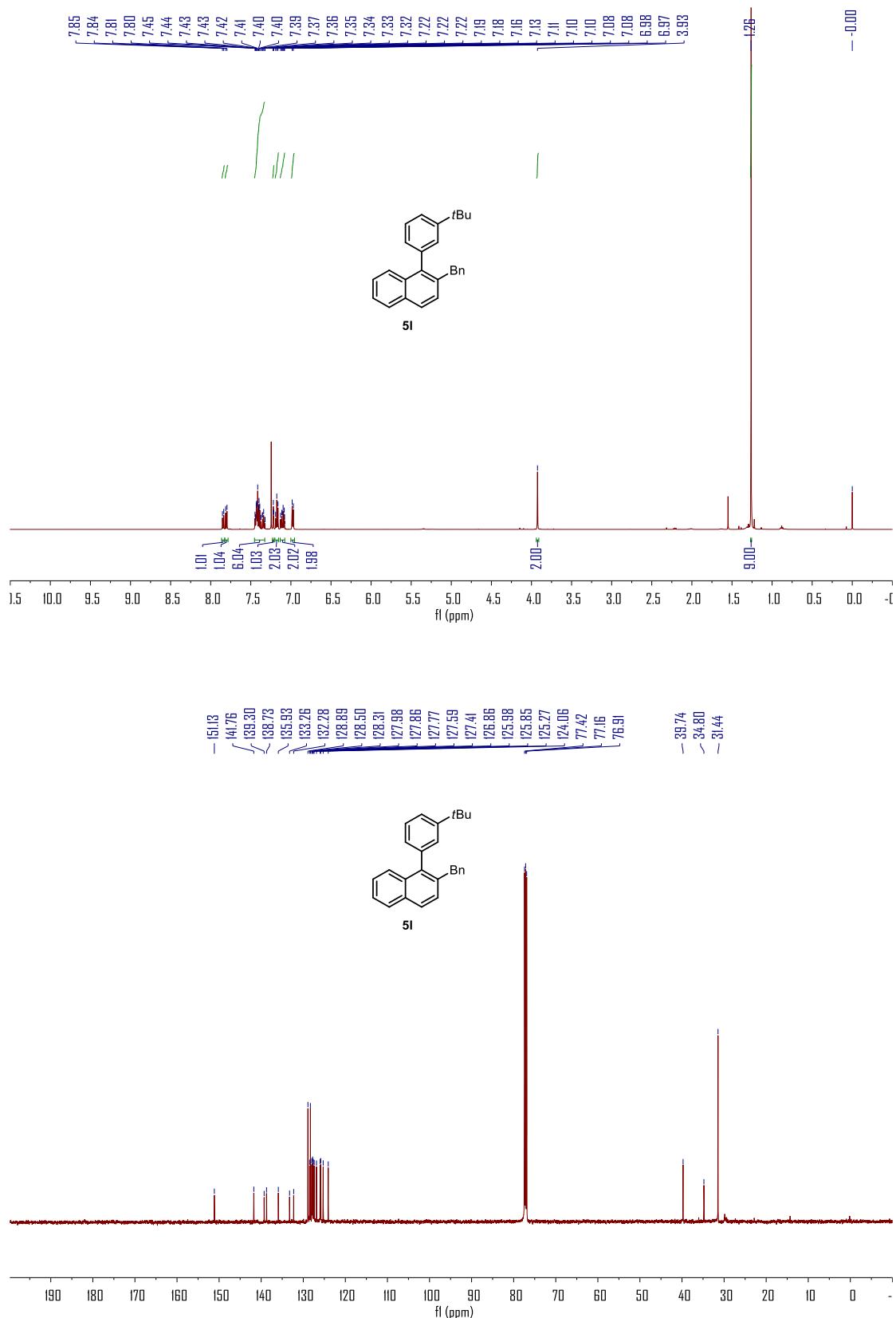
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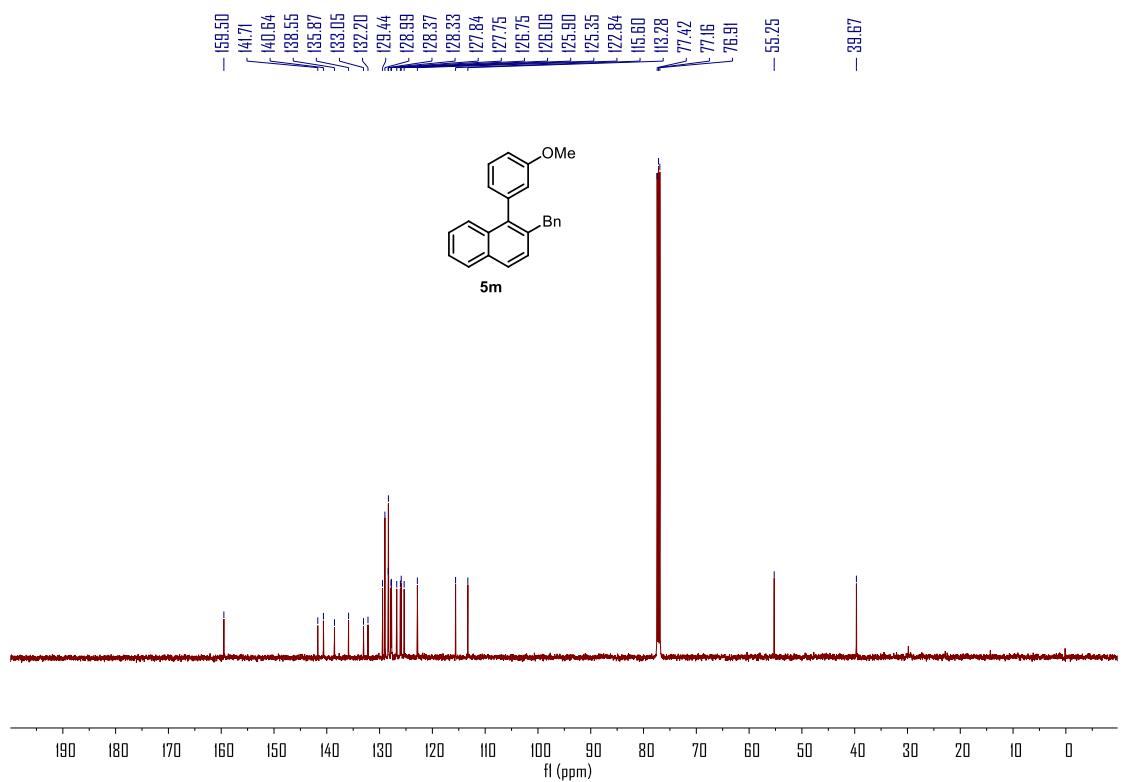
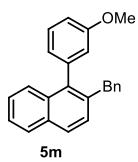
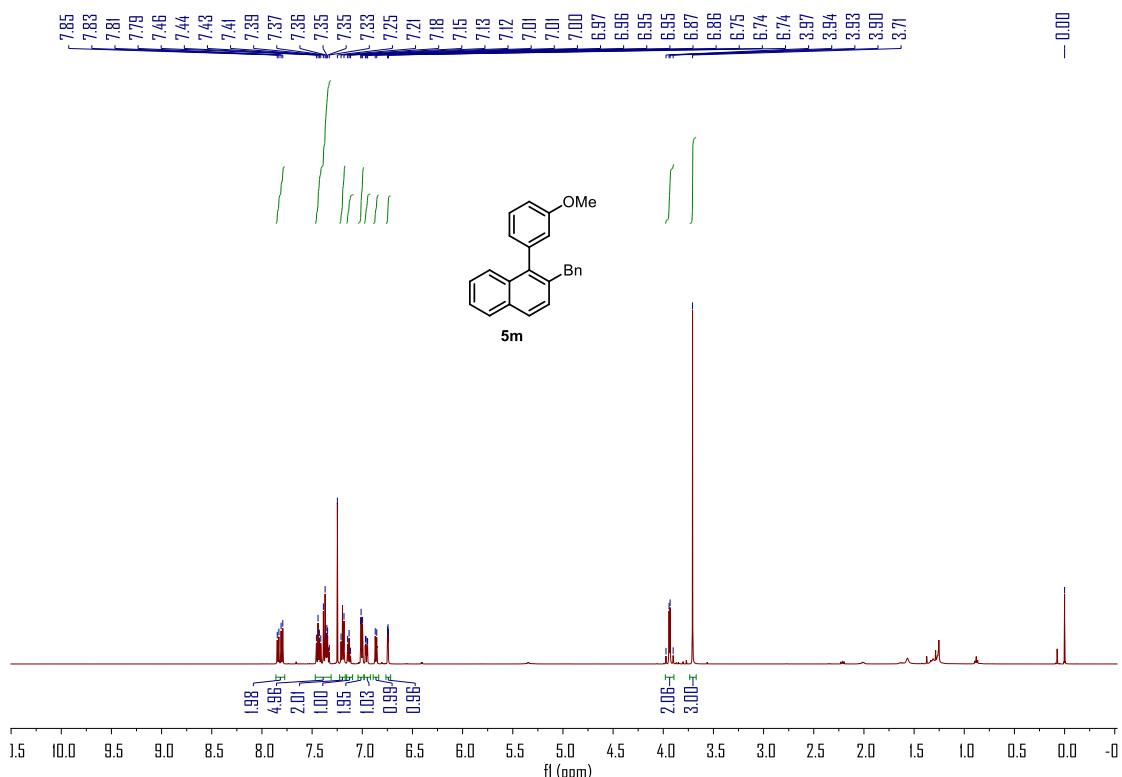


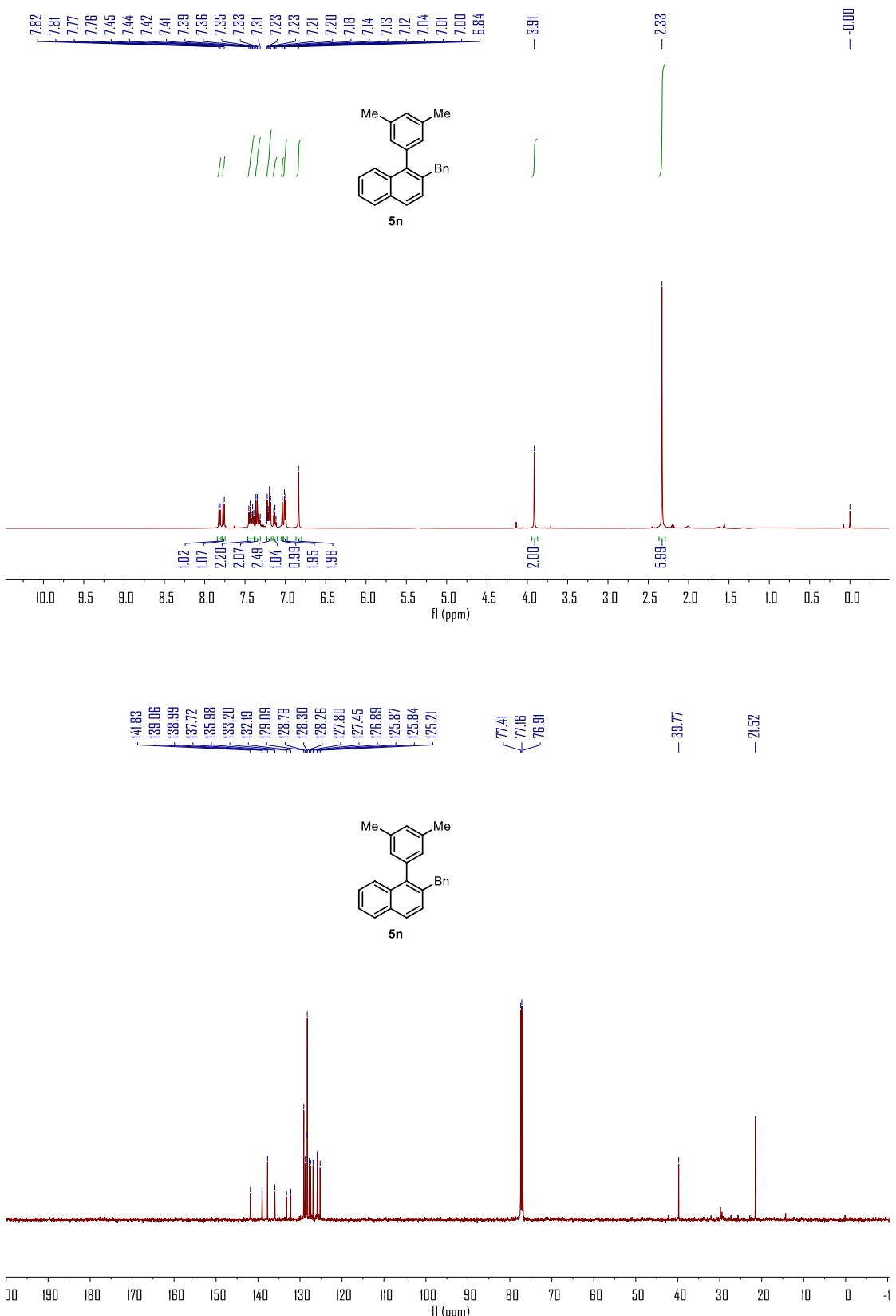
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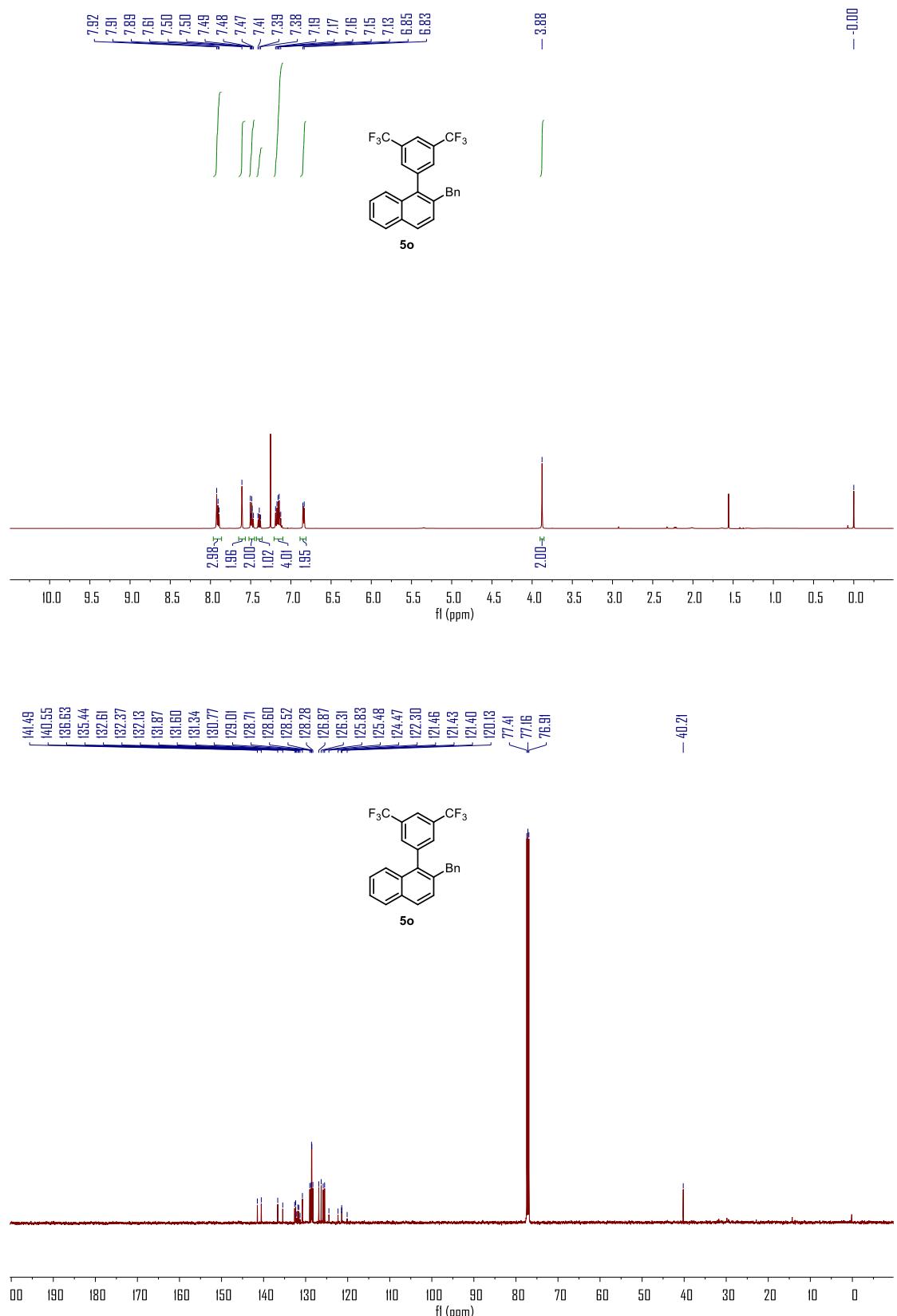


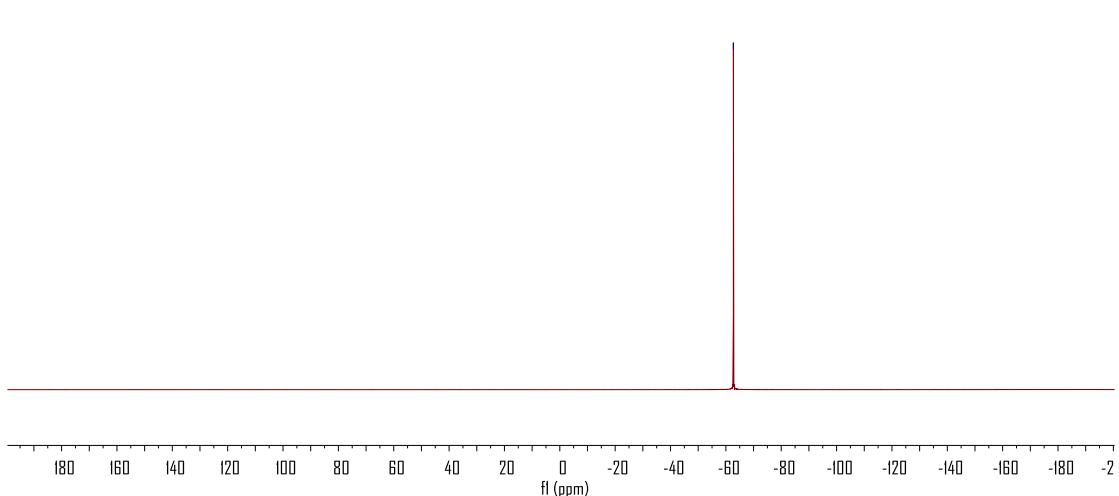
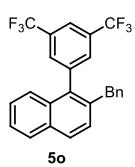


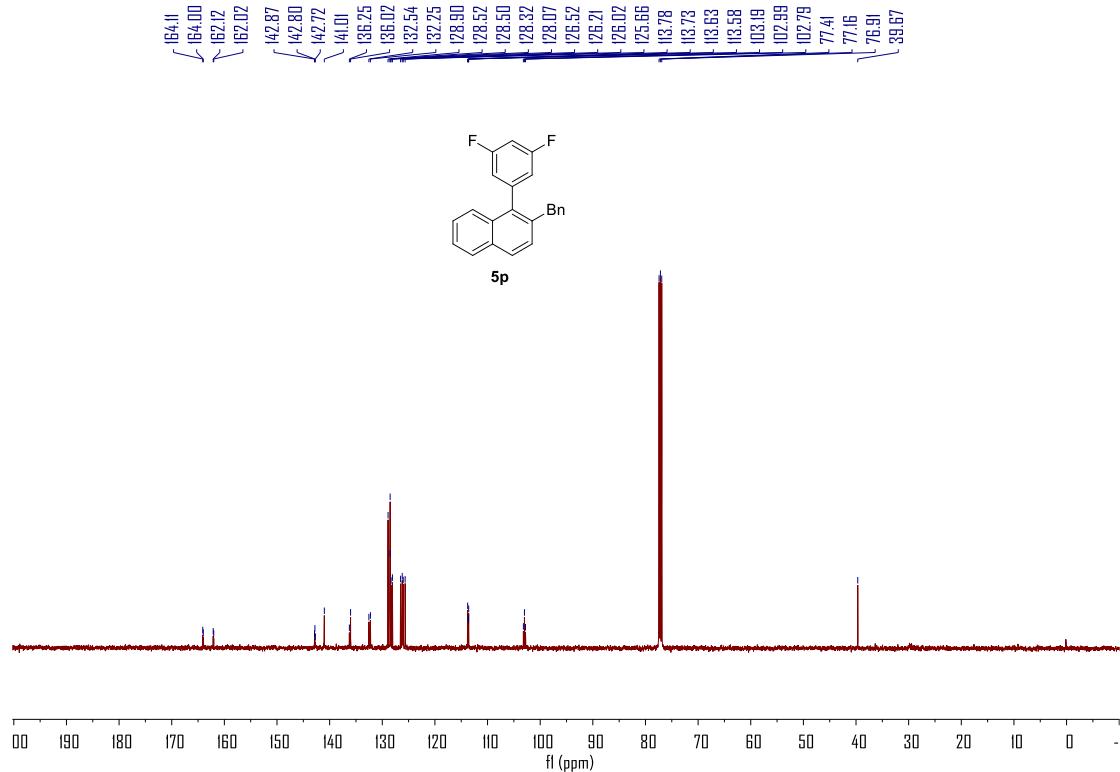
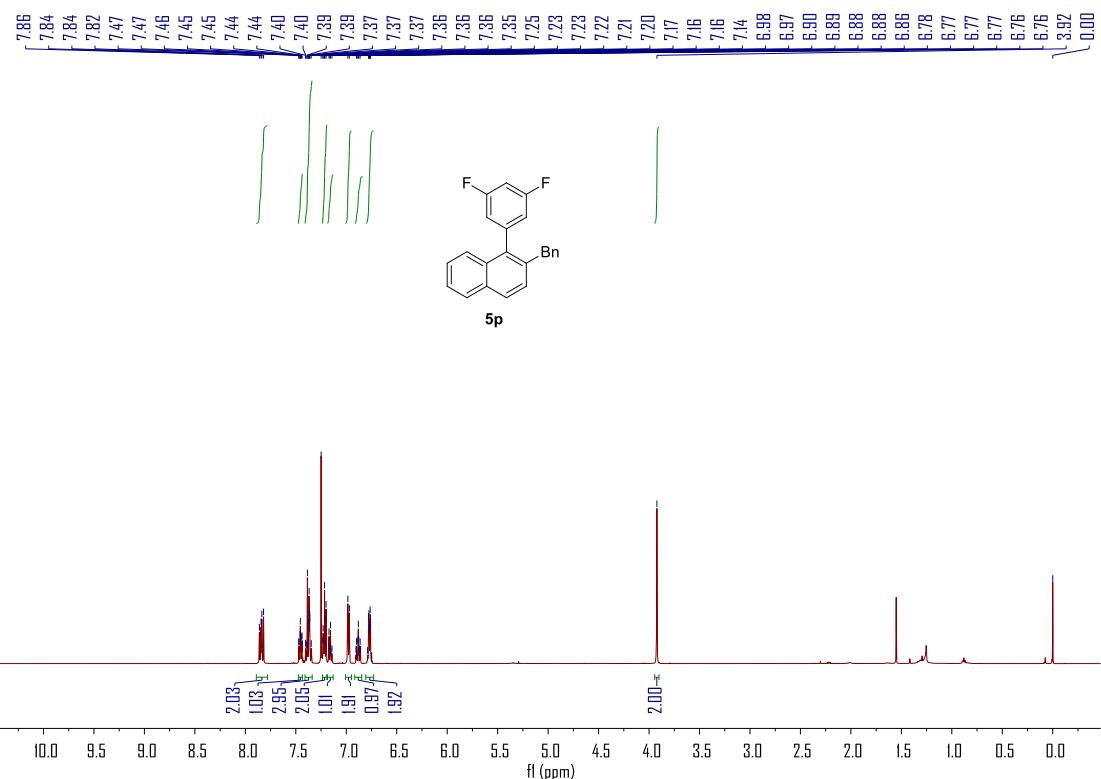








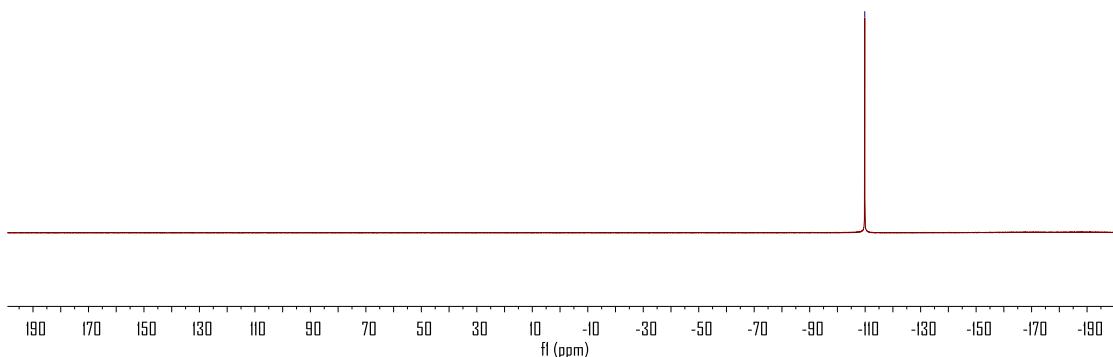


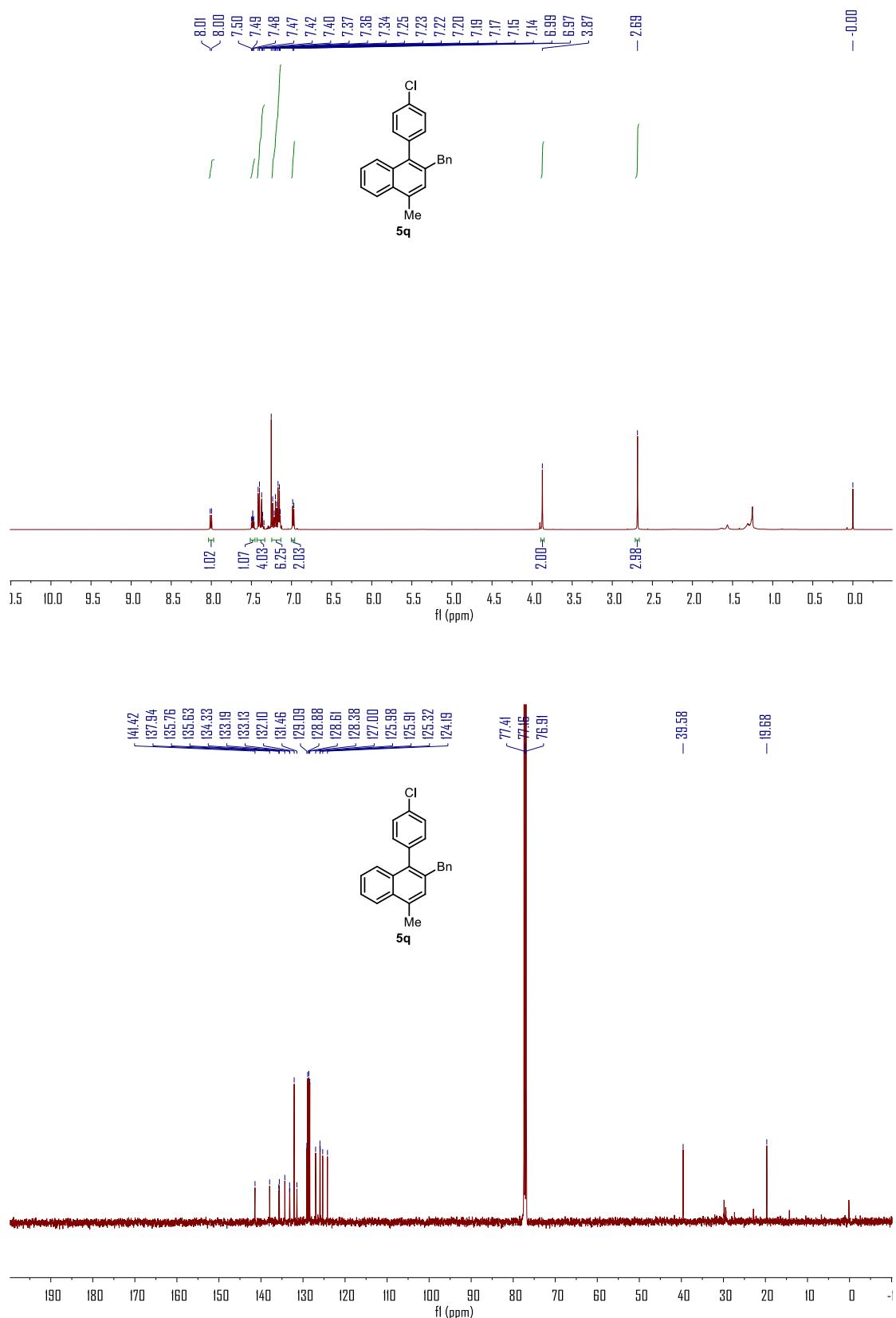


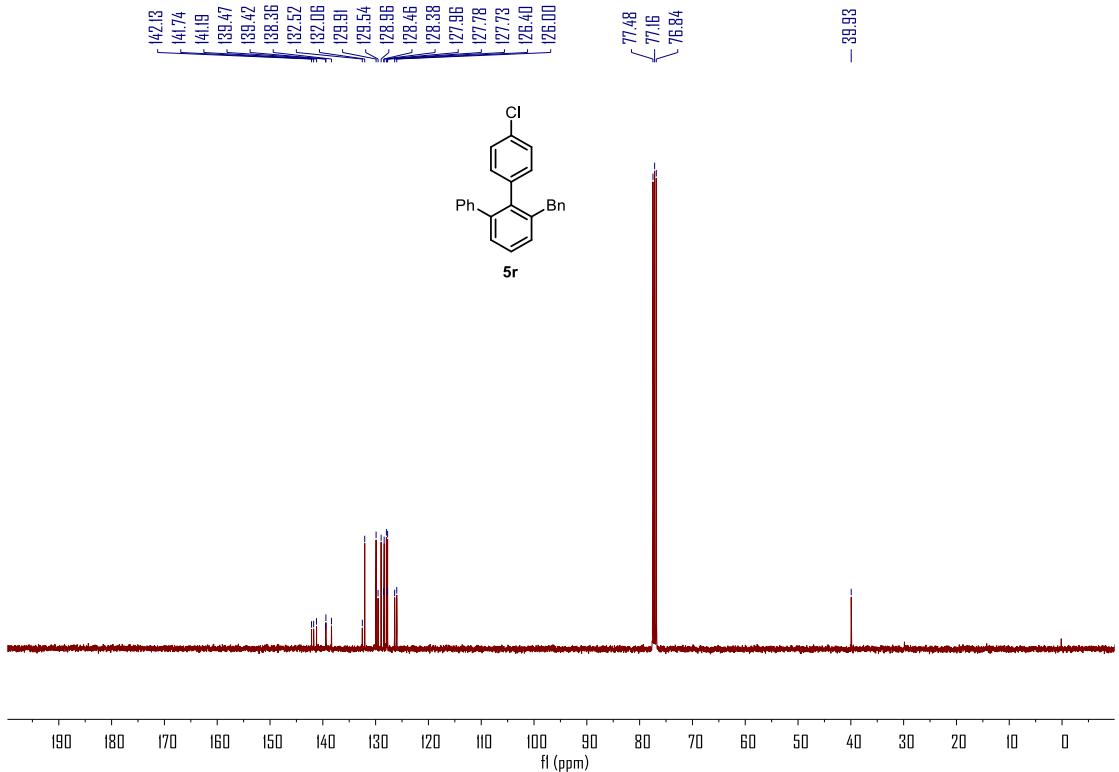
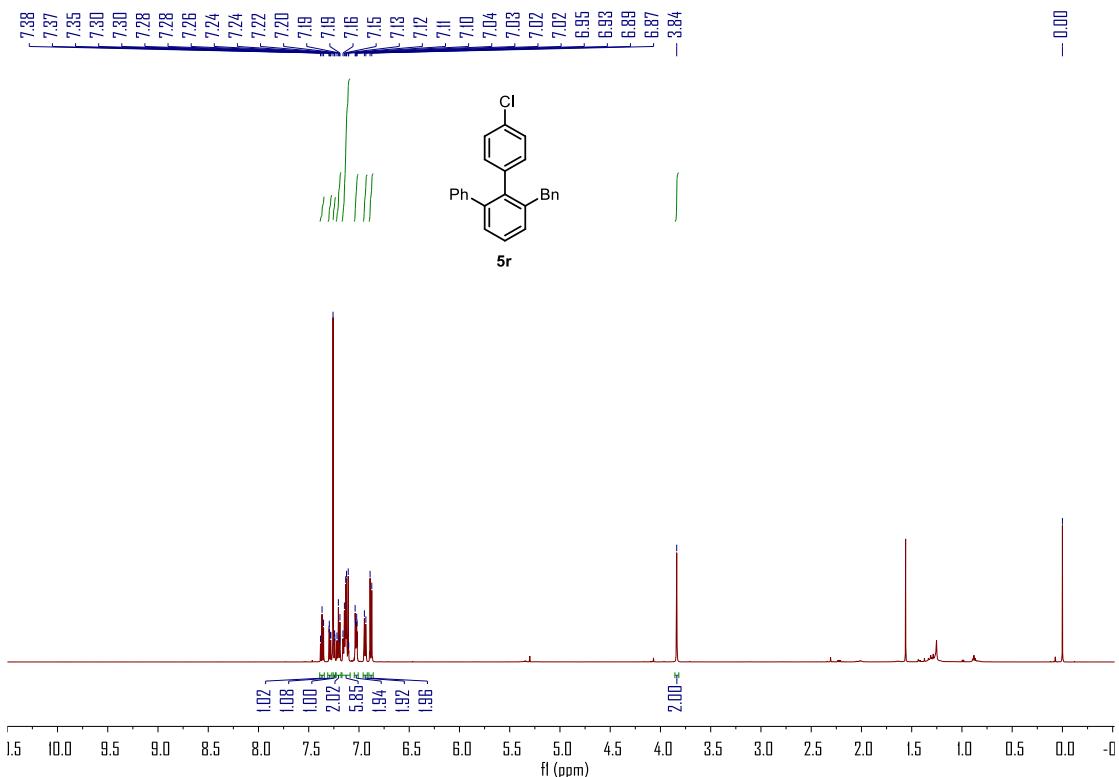
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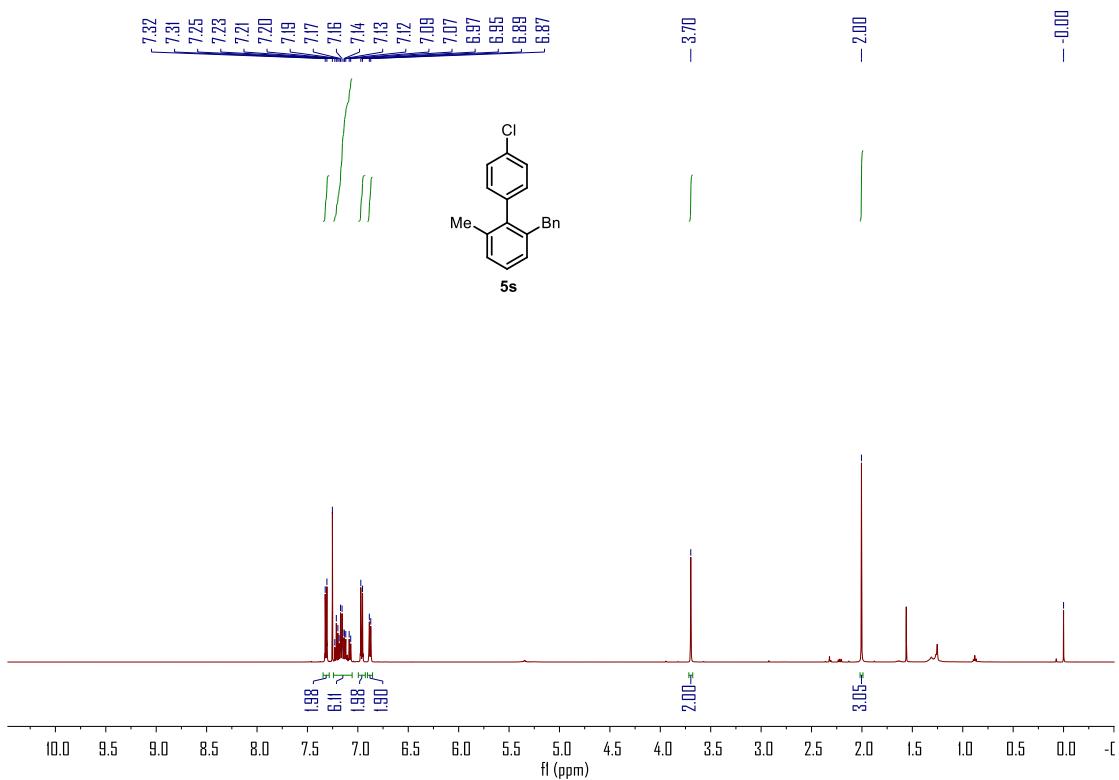


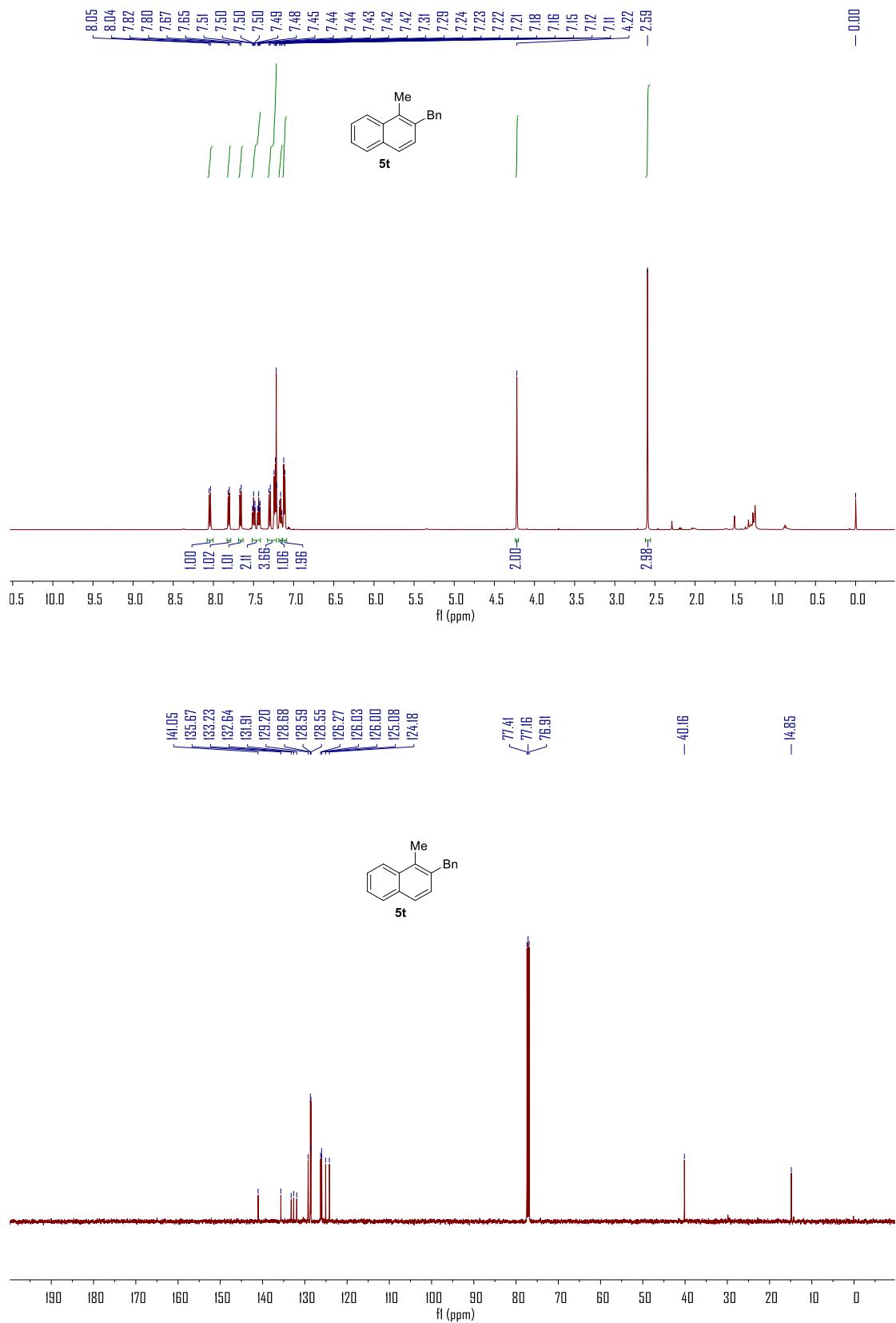
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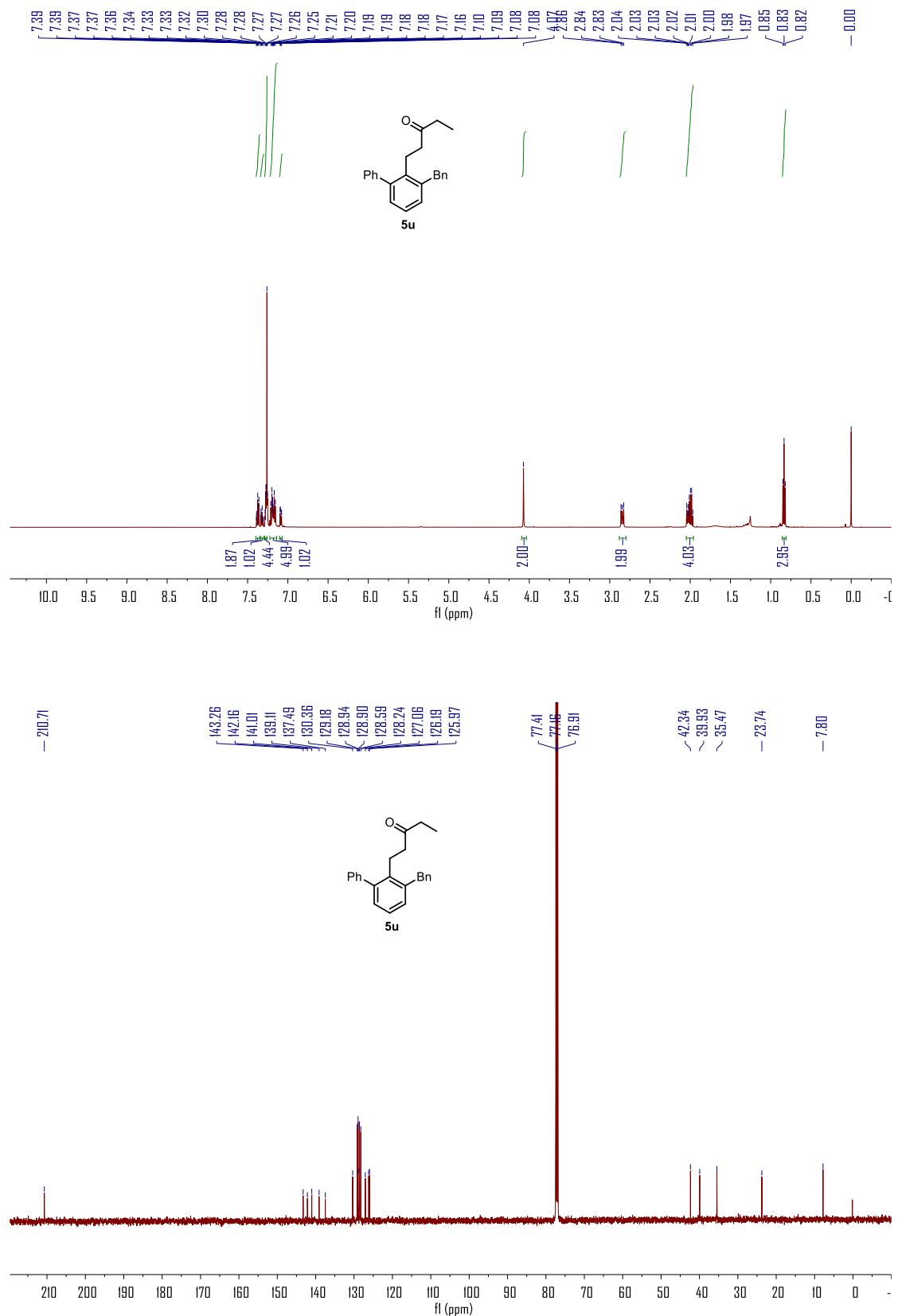


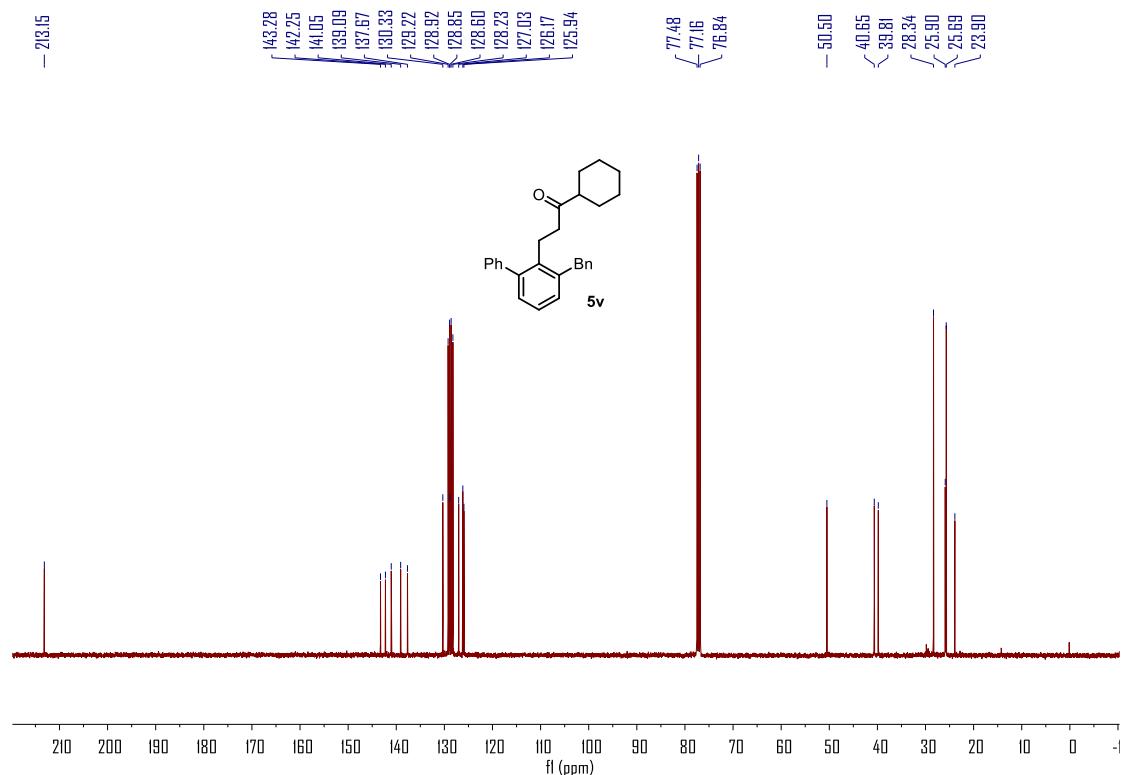
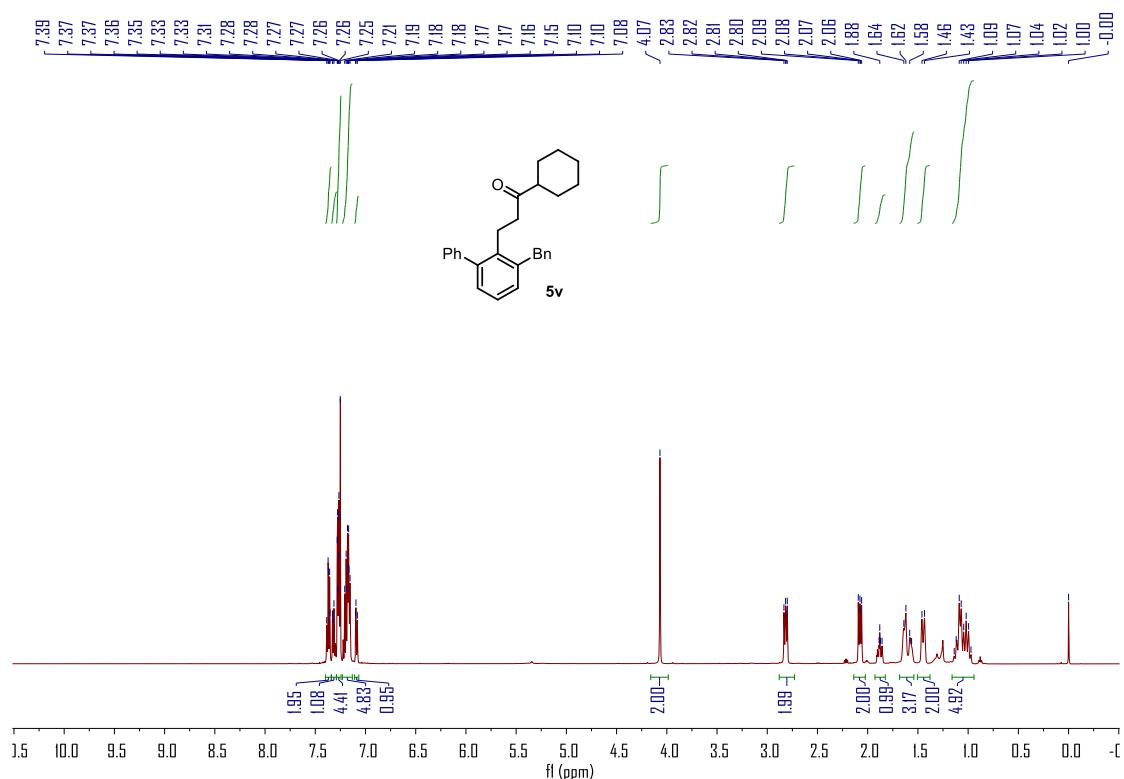


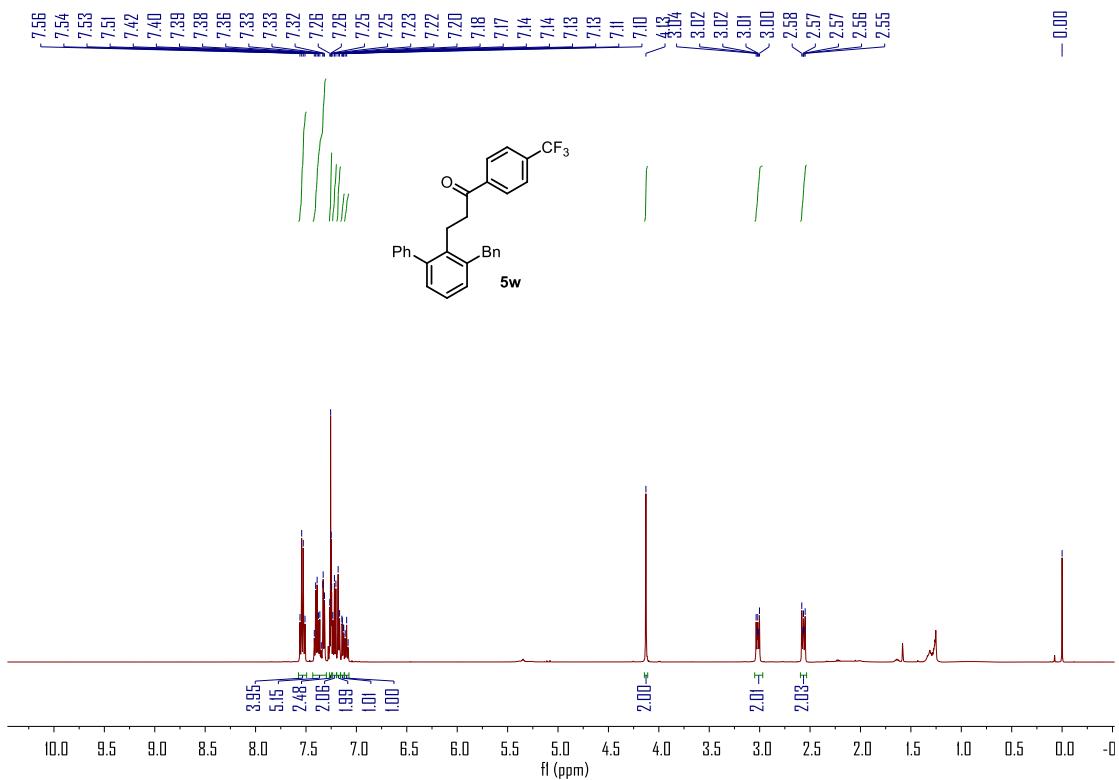


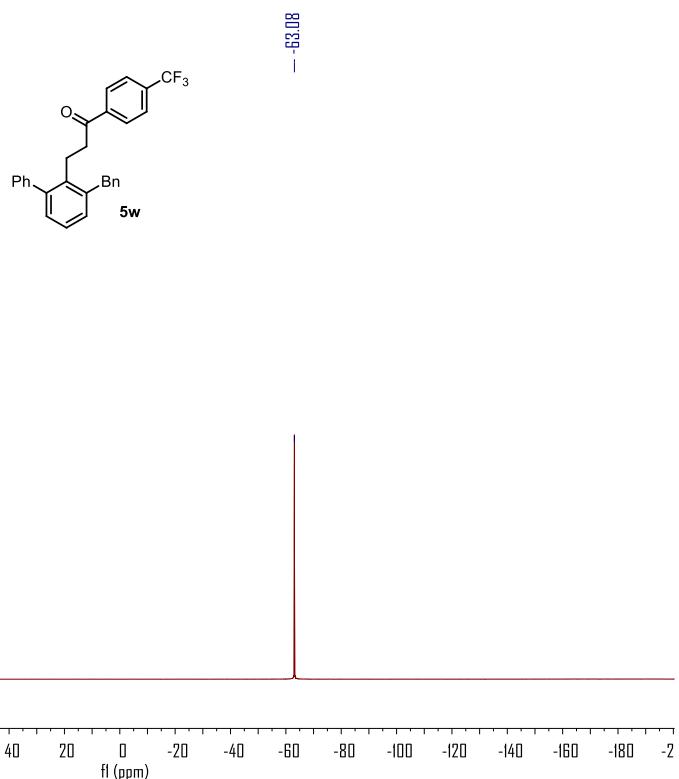


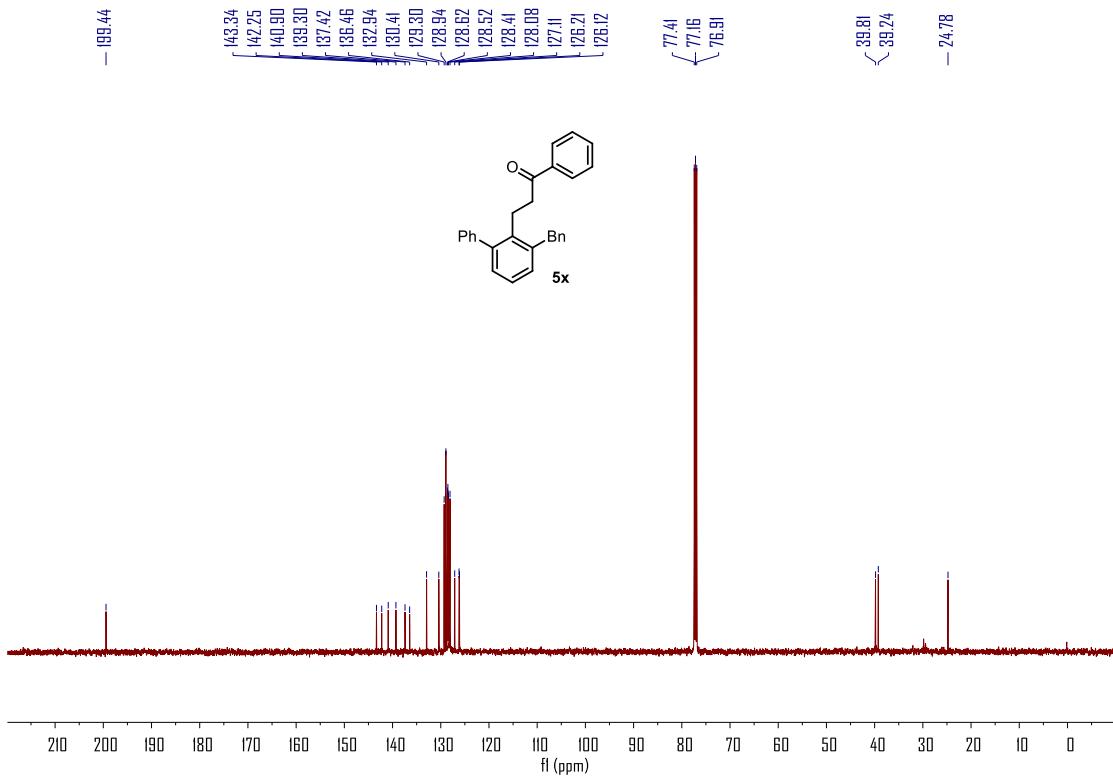
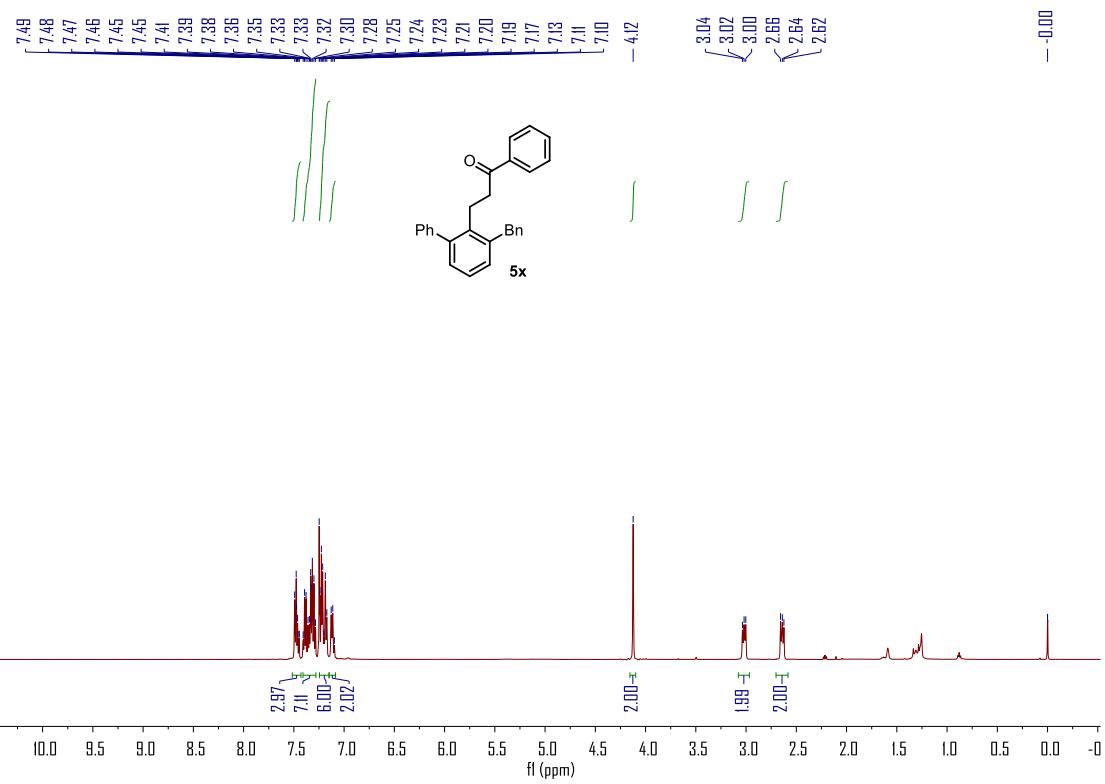


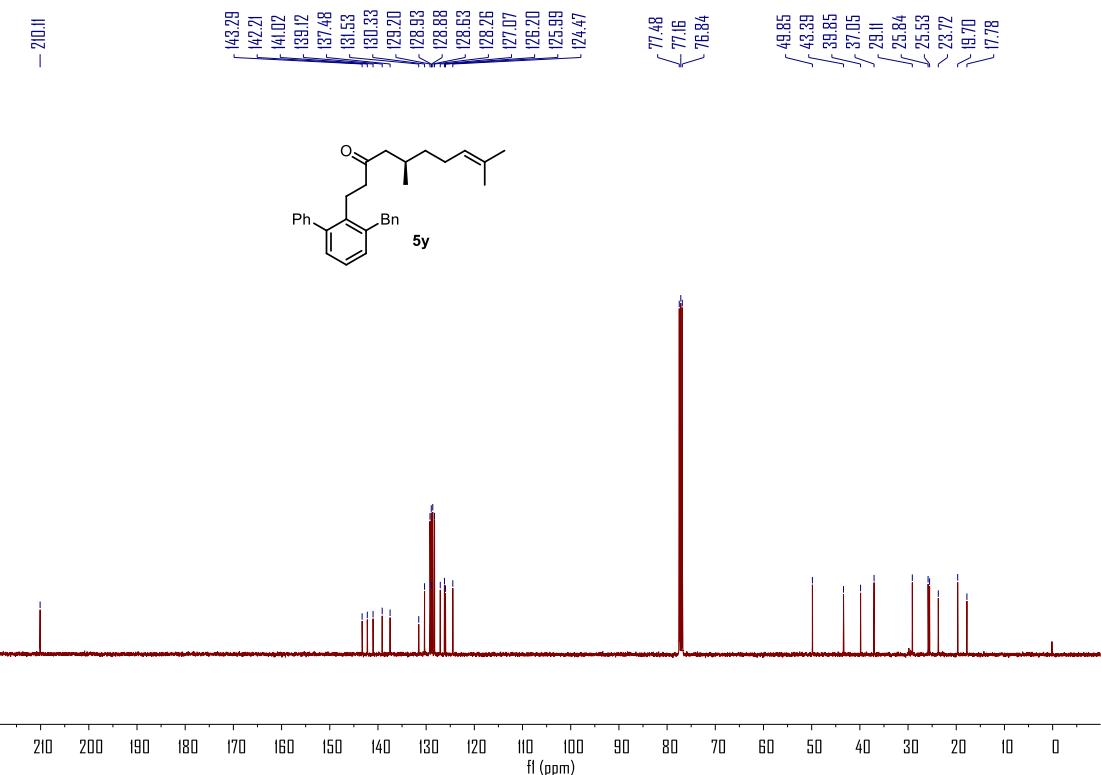
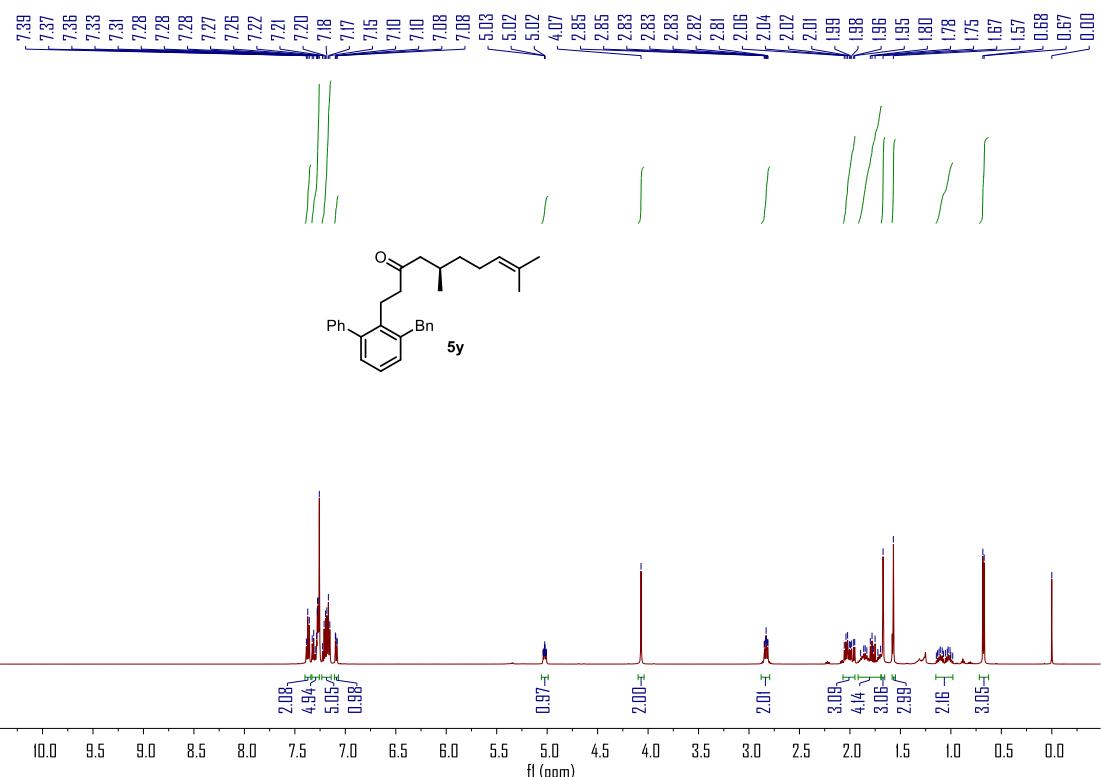


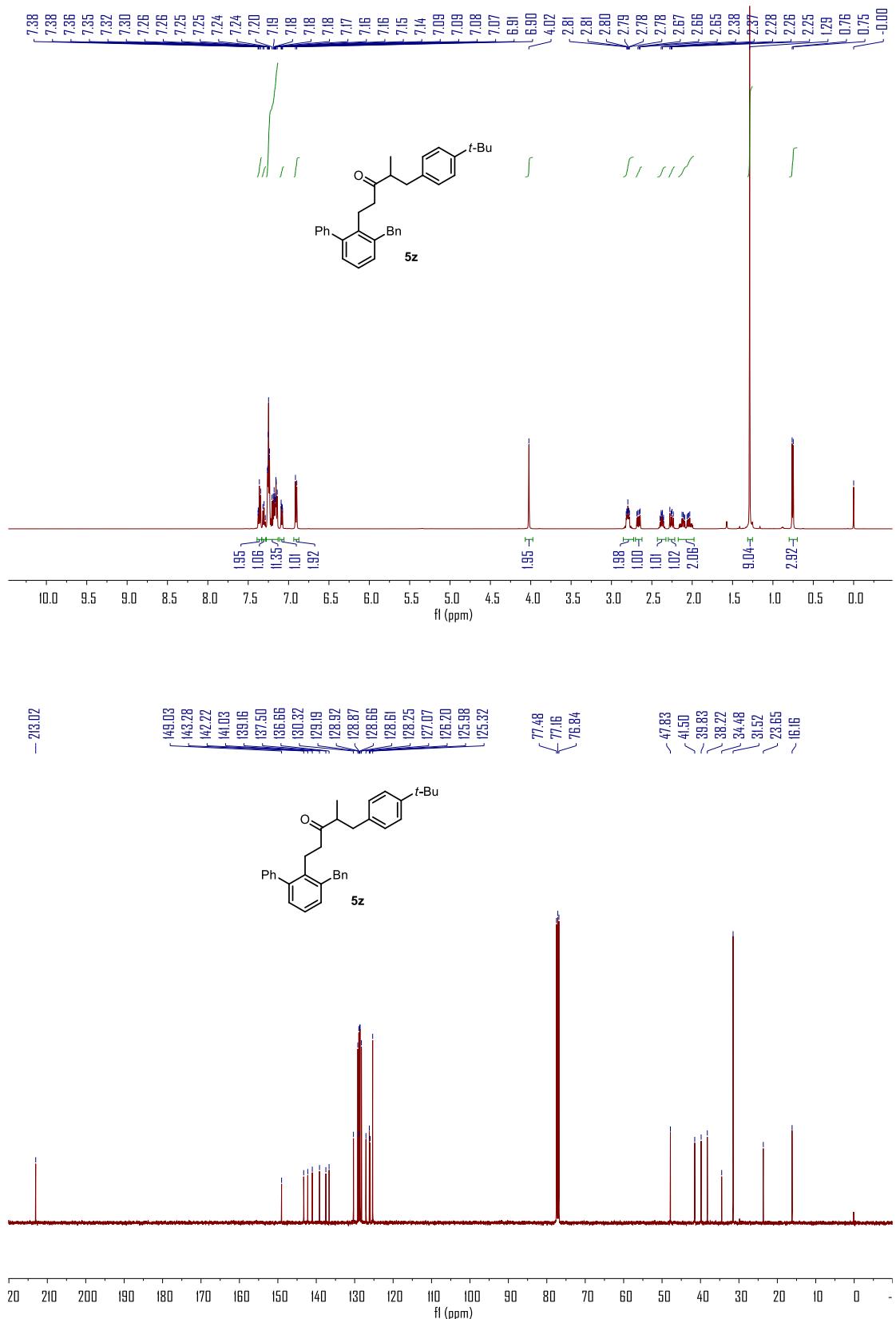


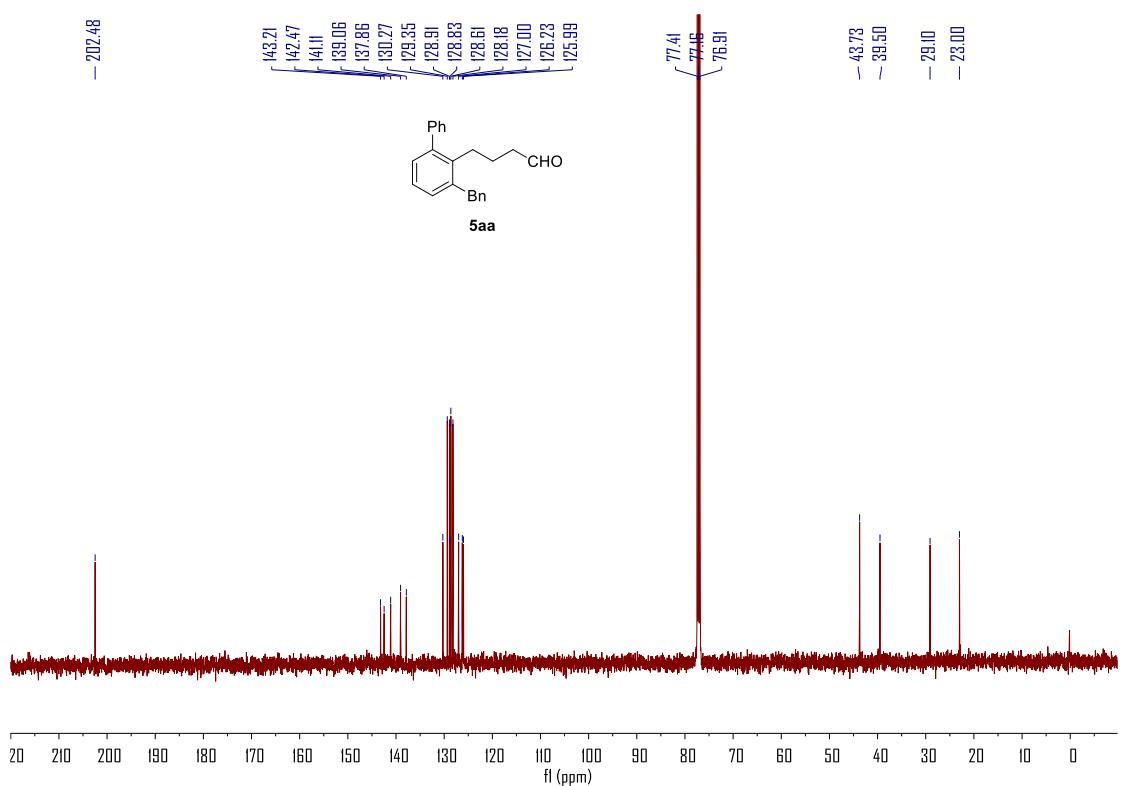
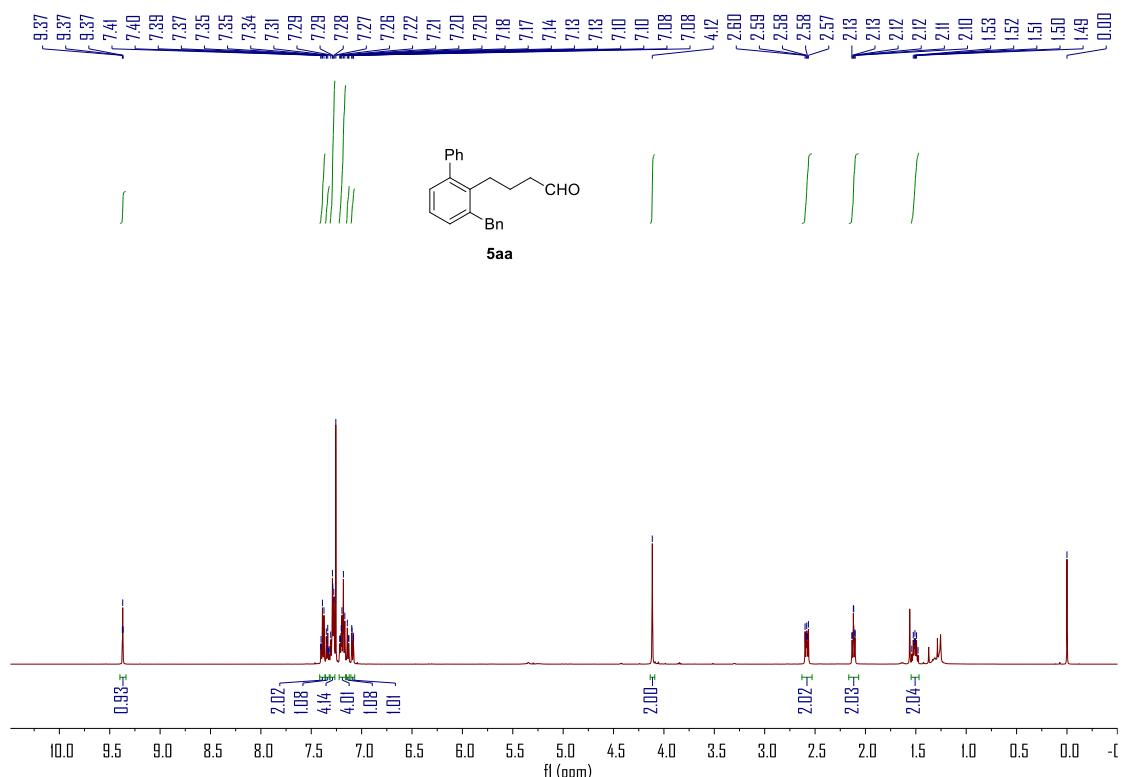


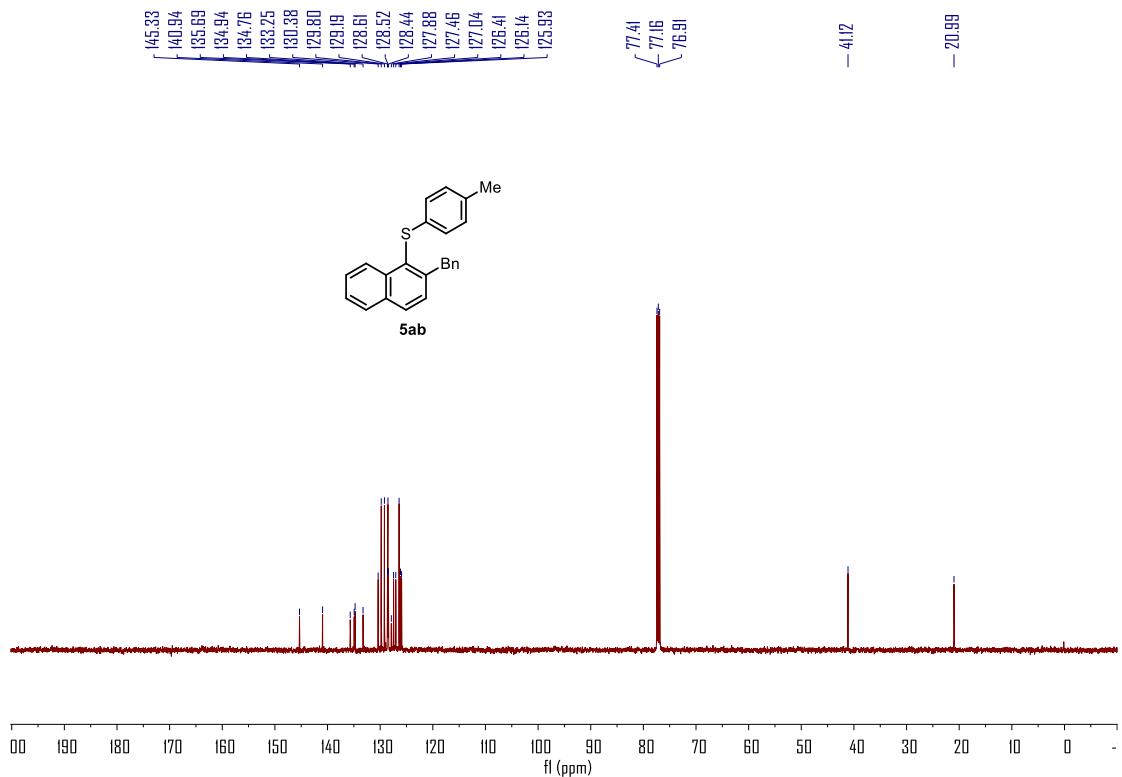
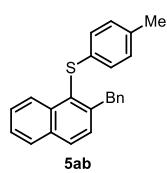
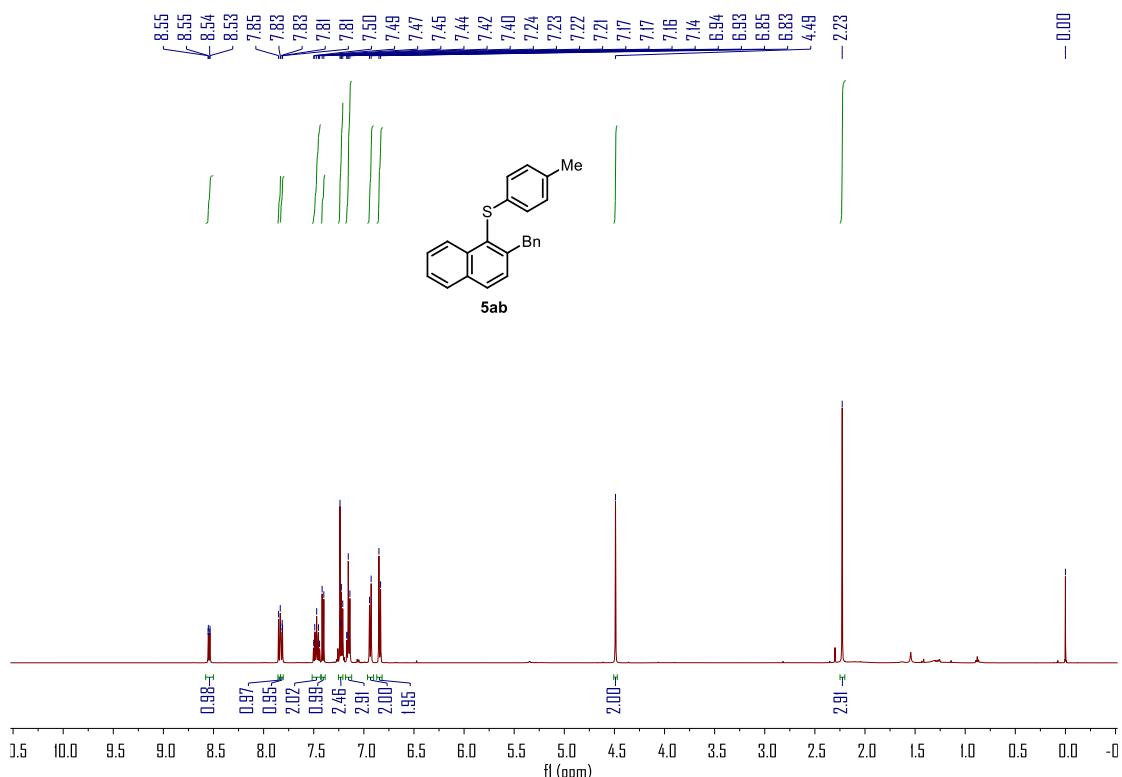


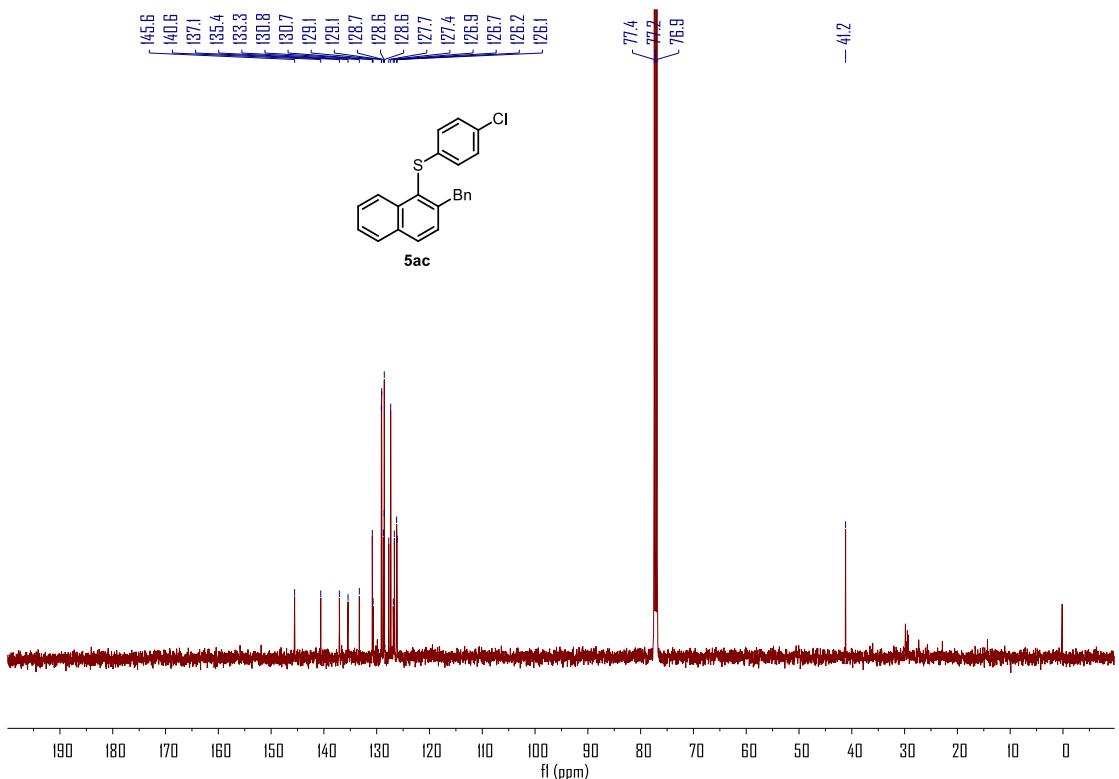
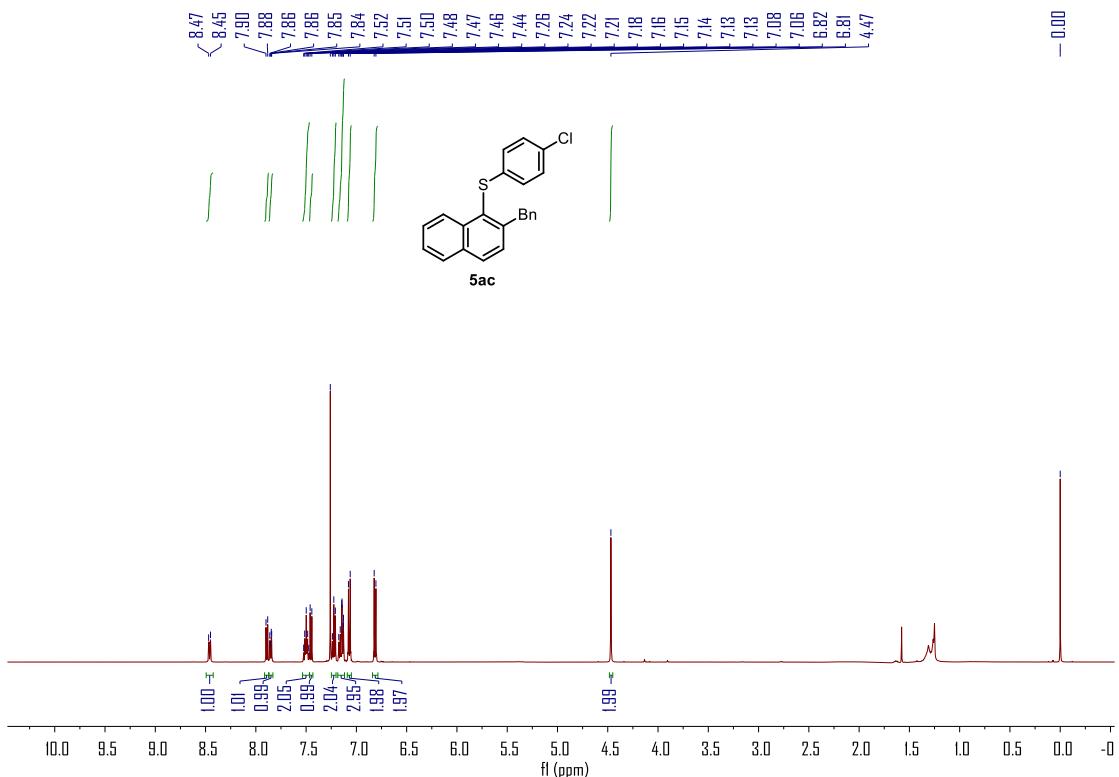


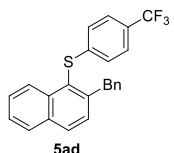
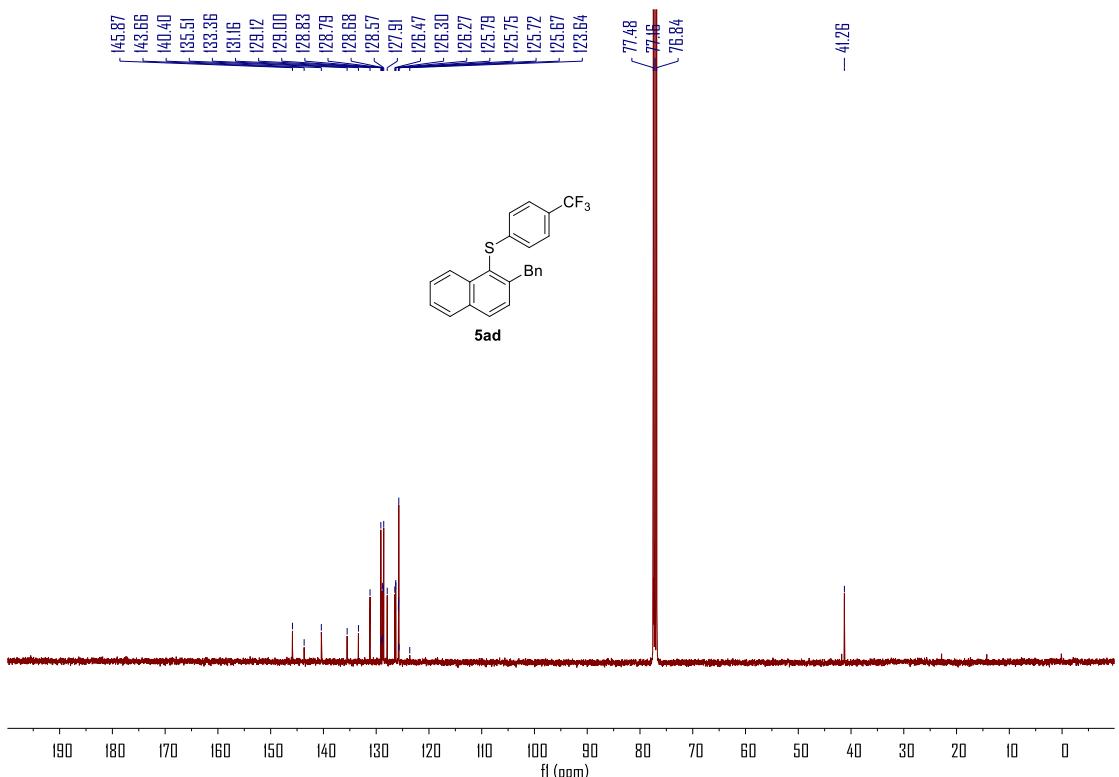
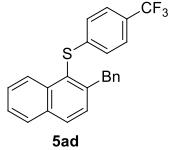
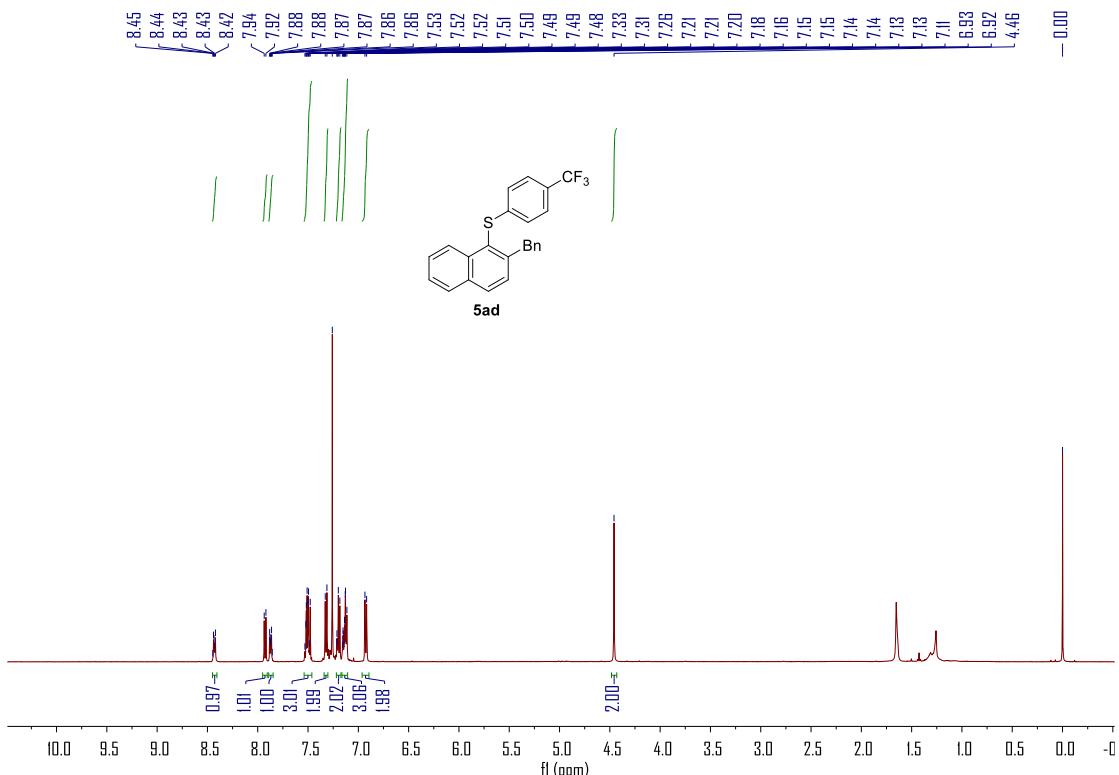












— -67.34

