

# **Iridium-Catalyzed 1,5-(Aryl)aminomethylation of 1,3-Enynes by Alkenyl-to-Allyl 1,4-Iridium(I) Migration**

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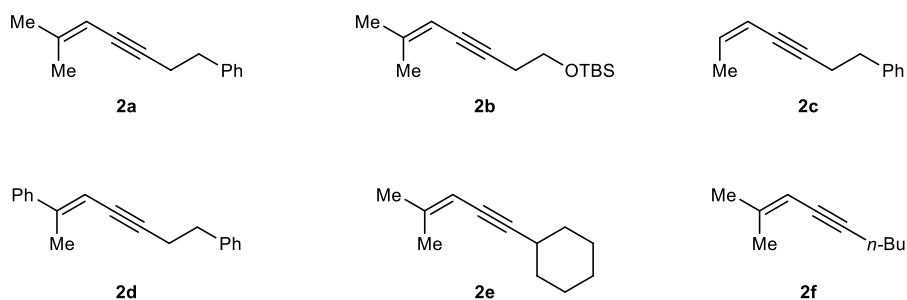
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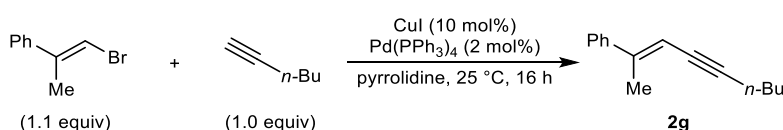
## General Information

All air-sensitive reactions were carried out under an argon atmosphere using oven-dried apparatus. Anhydrous 1,4-dioxane was purchased from Sigma Aldrich and was dried further over activated molecular sieves. All commercially available reagents were used as received unless otherwise stated. Arylboronic acids were used as received unless the sample contained >10% boroxine as determined by  $^1\text{H}$  NMR analysis. In this case, the boronic acid was stirred in a mixture of  $\text{Et}_2\text{O}$  and water for 30 min. The organic phase was separated, dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated *in vacuo* to give the corresponding boronic acid, which was used without further purification. All petroleum ether used was 40-60 °C petroleum ether. Thin layer chromatography (TLC) was performed on Merck DfAlufoilien 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Infra-red (IR) spectra were recorded on a Nicolet Avatar 360 FT instrument on compounds evaporated from  $\text{CHCl}_3$ . NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to external tetramethylsilane *via* the residual protonated solvent ( $^1\text{H}$ ) or the solvent itself ( $^{13}\text{C}$ ). All chemical shifts are reported in parts per million (ppm). For  $\text{CDCl}_3$ , the shifts are referenced to 7.26 ppm for  $^1\text{H}$  NMR spectroscopy and 77.16 ppm for  $^{13}\text{C}$  NMR spectroscopy. Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q (quartet), app (apparent), br (broad) and m (multiplet). Coupling constants ( $J$ ) are quoted to the nearest 0.1 Hz. HSQC and HMBC experiments were used to assist  $^1\text{H}$  NMR assignments where required.  $^{13}\text{C}$  NMR assignments were made using the DEPT sequence with secondary pulses at  $135^\circ$ .  $^{19}\text{F}$  NMR spectra were proton-decoupled and were referenced through the solvent lock ( $^2\text{H}$ ) signal according to IUPAC recommended secondary referencing method the Bruker protocols. High-resolution mass spectra were recorded using electrospray ionization (ESI) or electron impact ionization (EI) techniques.

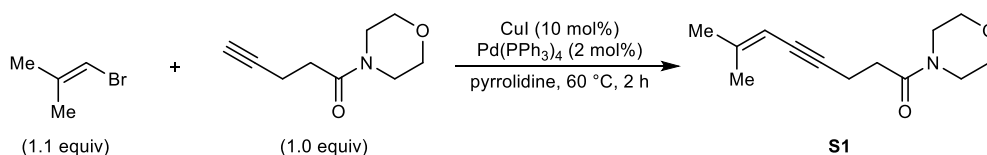
## Preparation of 1,3-Enynes



Known 1,3-enynes were prepared according to literature procedures: **2a-d**,<sup>1</sup> **2e**,<sup>2</sup> **2f**.<sup>3</sup>

*(E)*-Non-2-en-4-yn-2-ylbenzene (**2g**)

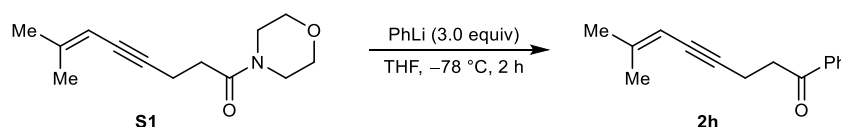
To a degassed solution of 1-bromo-2-phenylprop-1-ene<sup>4</sup> (1.60 g, 11.5 mmol) in pyrrolidine (30 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (250 mg, 0.22 mmol), followed by CuI (210 mg, 1.09 mmol). Hex-1-yne (1.41 g, 10.9 mmol) was then added and the mixture was stirred for 16 h under a nitrogen atmosphere. 1 M Aqueous HCl solution (10 mL) was added slowly and the product was extracted with Et<sub>2</sub>O (3 x 25 mL). The combined organic layers were washed with 1 M aqueous HCl solution (10 mL), dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. The mixture was purified by column chromatography (1% Et<sub>2</sub>O/petroleum ether) to give the *enyne* **2g** (910 mg, 4.59 mmol, 43%) as a colorless oil. *R*<sub>f</sub> = 0.57 (1% Et<sub>2</sub>O/petroleum ether); IR 2957, 2931, 2860, 2210, 1597, 1494, 1444, 1377, 1325, 1071, 1027, 910, 850, 753, 692, 615, 545, 480 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.44-7.40 (2H, m, ArH), 7.35-7.30 (2H, m, ArH), 7.29-7.26 (1H, m, ArH), 5.89-5.86 (1H, m, =CH), 2.43 (2H, td, *J* = 7.0, 2.2 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.29 (3H, d, *J* = 1.2 Hz, CH<sub>3</sub>C=), 1.63-1.56 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.52-1.45 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 0.95 (3H, t, *J* = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.8 (C), 141.4 (C), 128.5 (2 × CH), 127.9 (CH), 125.5 (2 × CH), 107.4 (CH), 96.6 (C), 79.2 (C), 31.2 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 19.6 (CH<sub>2</sub>), 18.5 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>).

7-Methyl-1-morpholinooct-6-en-4-yn-1-one (**S1**)

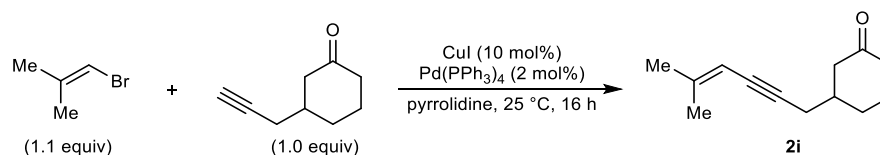
A solution of 1-bromo-2-methylprop-1-ene (667 mg, 4.94 mmol) in pyrrolidine (15 mL) was degassed with argon for 15 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.10 mmol) and CuI (94.0 mg, 0.49 mmol) were added followed by 1-morpholinopent-4-yn-1-one<sup>5</sup> (750 mg, 4.49 mmol). The resulting solution was

degassed for a further 10 min before being heated to 60 °C for 2 h. The black solution was diluted with saturated aqueous NH<sub>4</sub>Cl solution (20 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (40% EtOAc/petroleum ether) gave 1,3-*enyne* **S1** (795 mg, 3.59 mmol, 80%) as a yellow oil. *R*<sub>f</sub> = 0.59 (40% Et<sub>2</sub>O/petroleum ether); IR 2857, 1646 (C=O), 1435, 1301, 1272, 1225, 1116, 1021, 847 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.21 (1H, app dd, *J* = 2.5, 1.1 Hz, =CH), 3.69-3.65 (4H, m, CH<sub>2</sub>), 3.63 (2H, d, *J* = 5.0 Hz, CH<sub>2</sub>), 3.51-3.46 (2H, m, CH<sub>2</sub>), 2.70 (2H, ddd, *J* = 8.1, 6.8, 1.9 Hz, CH<sub>2</sub>), 2.60-2.53 (2H, m, CH<sub>2</sub>), 1.86 (3H, d, *J* = 1.1 Hz, CH<sub>3</sub>), 1.77 (3H, d, *J* = 1.5 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.1 (C), 147.6 (C), 105.3 (CH), 90.5 (C), 79.2 (C), 67.1 (CH<sub>2</sub>), 66.8 (CH<sub>2</sub>), 46.1 (CH<sub>2</sub>), 42.2 (CH<sub>2</sub>), 32.7 (CH<sub>2</sub>), 24.8 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 15.9 (CH<sub>2</sub>); HRMS (ESI) Exact mass calculated for C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 222.1489, found: 222.1490.

### 7-Methyl-1-phenyloct-6-en-4-yn-1-one (2h)



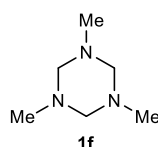
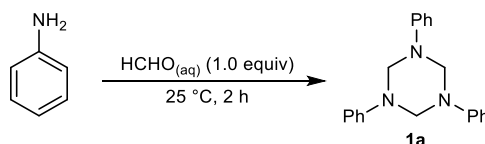
PhLi (1.58 M in dibutyl ether, 4.3 mL, 6.78 mmol) was added to a solution of **S1** (500 mg, 2.26 mmol) in THF (10 mL) at -78 °C. The resulting solution was stirred for 2 h, quenched carefully with saturated aqueous NH<sub>4</sub>Cl solution (15 mL), and extracted with Et<sub>2</sub>O (3 × 15 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (10% Et<sub>2</sub>O/petroleum ether) gave 1,3-*enyne* **2h** (437 mg, 2.06 mmol, 91%) as a yellow oil. *R*<sub>f</sub> = 0.35 (10% Et<sub>2</sub>O/petroleum ether); IR 2911, 2330 (C≡C), 1681 (C=O), 1578, 1447, 1409, 1360, 1290, 1203, 1046, 971, 821, 739, 689, 655, 567, 539, 489 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00-7.95 (2H, m, ArH), 7.60-7.54 (1H, m, ArH), 7.47 (2H, dd, *J* = 8.4, 7.1 Hz, ArH), 5.22 (1H, dt, *J* = 2.5, 1.1 Hz, =CH), 3.32-3.17 (2H, m, CH<sub>2</sub>), 2.78 (2H, td, *J* = 7.5, 2.1 Hz, CH<sub>2</sub>), 1.85 (3H, s, CH<sub>3</sub>), 1.77 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 198.3 (C), 147.5 (C), 136.8 (C), 133.3 (CH), 128.8 (2 × CH), 128.2 (2 × CH), 105.3 (CH), 90.6 (C), 79.1 (C), 38.3 (CH<sub>2</sub>), 24.8 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 14.6 (CH<sub>2</sub>); HRMS (ESI) Exact mass calculated for C<sub>15</sub>H<sub>17</sub>O [M+H]<sup>+</sup>: 213.1274, found: 213.1277.

**3-(5-Methylhex-4-en-2-yn-1-yl)cyclohexan-1-one (2i)**

A solution of 3-(prop-2-yn-1-yl)cyclohexan-1-one<sup>6</sup> (378 mg, 2.76 mmol) in pyrrolidine (2 mL) was added to a mixture of 1-bromo-2-methylprop-1-ene (412 mg, 3.05 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (65.0 mg, 0.06 mmol) and CuI (53.0 mg, 0.28 mmol) in pyrrolidine (5 mL) under an atmosphere of argon. The resulting solution was stirred at room temperature for 18 h, quenched with saturated aqueous NH<sub>4</sub>Cl solution (5 mL), extracted with Et<sub>2</sub>O (3 × 5 mL), and the combined organic layers were washed with brine (10 mL), dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (10% Et<sub>2</sub>O/petroleum ether) gave *enyne* **2i** (434 mg, 2.28 mmol, 83%) as a colorless oil. *R*<sub>f</sub> = 0.15 (10% Et<sub>2</sub>O/petroleum ether); IR 2929, 1710 (C=O), 1447, 1429, 1335, 1223, 1203, 1167, 1055, 868, 820, 732, 502, 488 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.28-5.17 (1H, m, =CH), 2.51-2.44 (1H, m, CH<sub>2</sub>), 2.42-2.31 (3H, m, CH<sub>2</sub>), 2.31-2.16 (2H, m, CH<sub>2</sub>), 2.10-1.92 (3H, m, CH and CH<sub>2</sub>), 1.86 (3H, s, CH<sub>3</sub>), 1.78 (3H, d, *J* = 1.4 Hz, CH<sub>3</sub>), 1.72-1.64 (1H, m, CH<sub>2</sub>), 1.62-1.45 (1H, m, CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 211.6 (C), 147.5 (C), 105.3 (CH), 88.8 (C), 80.8 (C), 47.4 (CH<sub>2</sub>), 41.3 (CH<sub>2</sub>), 38.5 (CH), 30.6 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 24.8 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>); HRMS (ESI) Exact mass calculated for C<sub>13</sub>H<sub>19</sub>O [M+H]<sup>+</sup>: 191.1430, found: 191.1436.

**Preparation of Triazinanes**

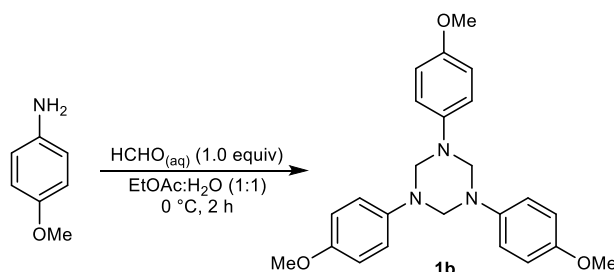
Triazinane **1f** is commercially available.

**1,3,5-Triphenyl-1,3,5-triazinane (1a)**

A solution of aniline (5.00 mL, 54.9 mmol) and aqueous formaldehyde (37%, 4.20 mL, 54.9 mmol) was stirred at room temperature for 2 h. Et<sub>2</sub>O (10 mL) and H<sub>2</sub>O (10 mL) were added and the resulting precipitate was filtered. The solid was then washed with petroleum ether (10 mL) to give triazinane **1a** (3.58 g, 11.3 mmol, 21%) as an off-white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25-7.18 (6H, m, ArH), 7.06-7.01 (6H, m, ArH), 6.87 (3H, tt, *J* = 7.3, 1.1 Hz, ArH), 4.90 (6H, s, 3 × CH<sub>2</sub>); <sup>13</sup>C NMR

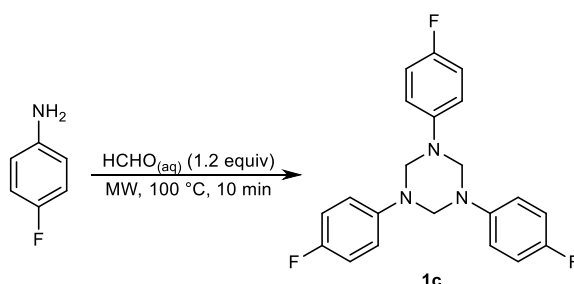
(101 MHz, CDCl<sub>3</sub>)  $\delta$  148.6 (3  $\times$  C), 129.2 (6  $\times$  CH), 120.9 (3  $\times$  CH), 117.7 (6  $\times$  CH), 68.6 (3  $\times$  CH<sub>2</sub>). These data are consistent with those reported previously.<sup>7</sup>

### 1,3,5-Tris(4-methoxyphenyl)-1,3,5-triazinane (**1b**)

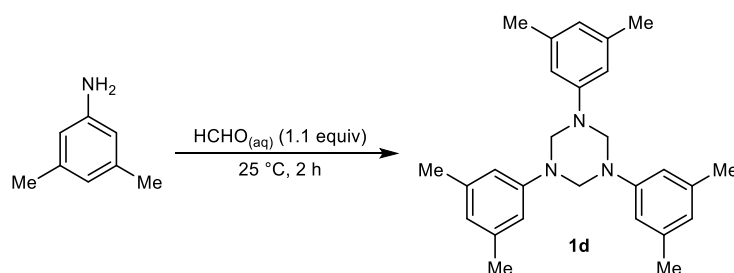


Aqueous formaldehyde (37%, 0.84 mL, 11 mmol) was added to a solution of *p*-anisidine (1.23 g, 10.0 mmol) in EtOAc (15 mL) and H<sub>2</sub>O (15 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, warmed to room temperature and then stirred for an additional 1 h. The resulting solid was filtered and washed with H<sub>2</sub>O to give triazinane **1b** (993 mg, 2.45 mmol, 25%) as a grey solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.05-6.99 (6H, m, ArH), 6.83-6.76 (6H, m, ArH), 4.69 (6H, s, 3  $\times$  CH<sub>2</sub>), 3.76 (9H, s, 3  $\times$  CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.5 (3  $\times$  C), 142.6 (3  $\times$  C), 120.1 (6  $\times$  CH), 114.4 (6  $\times$  CH), 71.1 (3  $\times$  CH<sub>2</sub>), 55.5 (3  $\times$  CH<sub>3</sub>). These data are consistent with those reported previously.<sup>8</sup>

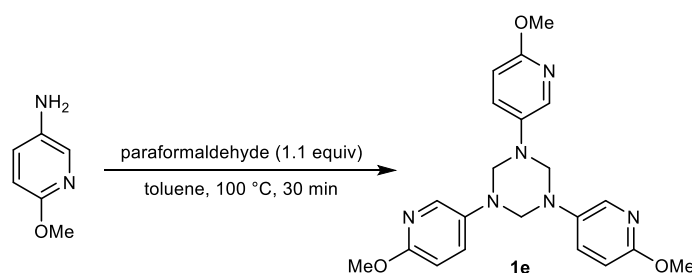
### 1,3,5-Tris(4-fluorophenyl)-1,3,5-triazinane (**1c**)



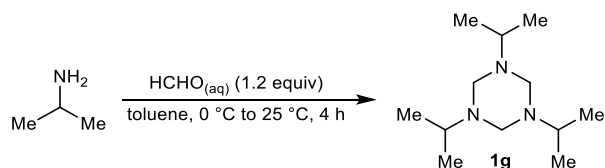
*para*-Fluoroaniline (0.95 mL, 10.0 mmol) and aqueous formaldehyde (37%, 0.9 mL, 12.0 mmol) were added to a sealed vessel and irradiated in a Biotage Initiator microwave synthesizer at 100 °C for 10 min. A solid formed upon standing, which was filtered and recrystallized from *iso*-hexane (MP = 157-162 °C) to give triazinane **1c** as a white solid (730 mg, 1.98 mmol, 20%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.00-6.95 (6H, m, ArH), 6.92-6.87 (6H, m, ArH), 4.76 (6H, s, 3  $\times$  CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  158.1 (d, *J*<sub>C-F</sub> = 240.8 Hz, C), 145.2 (d, *J*<sub>C-F</sub> = 2.6 Hz, C), 120.1 (d, *J*<sub>C-F</sub> = 7.7 Hz, 6  $\times$  CH), 115.8 (d, *J*<sub>C-F</sub> = 22.1 Hz, 6  $\times$  CH), 70.7 (3  $\times$  CH<sub>2</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -122.3 (s). These data are consistent with those reported previously.<sup>9</sup>

**1,3,5-Tris(3,5-dimethylphenyl)-1,3,5-triazinane (1d)**

A solution of 3,5-dimethylaniline (606 mg, 5.0 mmol) and aqueous formaldehyde (37%, 0.42 mL, 5.50 mmol) was stirred at 25 °C for 2h. Et<sub>2</sub>O (10 mL) and H<sub>2</sub>O (10 mL) was added and the resulting precipitate was filtered. The solid was then washed with petroleum ether (10 mL) to give triazinane **1d** (190 mg, 0.49 mmol, 10%) as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.62 (6H, s, ArH), 6.54 (3H, s, ArH), 4.77 (6H, s, 3 × CH<sub>2</sub>), 2.25 (18H, s, 6 × CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.9 (3 × C), 138.8 (6 × C), 122.8 (3 × CH), 115.7 (6 × CH), 68.7 (3 × CH<sub>2</sub>), 21.8 (6 × CH<sub>3</sub>). These data are consistent with those reported previously.<sup>9</sup>

**1,3,5-Tris(6-methoxypyridin-3-yl)-1,3,5-triazinane (1e)**

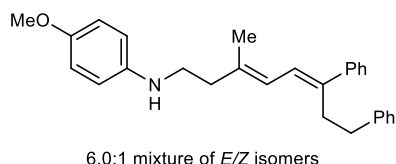
Paraformaldehyde (532 mg, 17.7 mmol) was added to a solution of 5-amino-2-methoxypyridine (2.00 g, 16.1 mmol) in toluene (20 mL) and the mixture was heated at 110 °C for 30 min. The reaction was cooled to room temperature and concentrated *in vacuo*. Petroleum ether (20 mL) was added, and the resulting solid was isolated by filtration and washed with additional petroleum ether to leave triazinane **1e** (1.64 g, 4.02 mmol, 25%) as a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (3H, dd, *J* = 3.0, 0.7 Hz, ArH), 7.39 (3H, dd, *J* = 8.9, 3.0 Hz, ArH), 6.61 (3H, dd, *J* = 8.9, 0.7 Hz, ArH), 4.72 (6H, s, 3 × CH<sub>2</sub>), 3.87 (9H, s, 3 × CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6 (3 × C), 139.2 (3 × C), 137.0 (3 × CH), 131.3 (3 × CH), 110.9 (3 × CH), 70.9 (3 × CH<sub>2</sub>), 53.4 (3 × CH<sub>3</sub>). These data are consistent with those reported previously.<sup>8</sup>

**1,3,5-Triisopropyl-1,3,5-triazinane (1g)**

A solution of isopropylamine (5.00 mL, 58.8 mmol) in toluene (15 mL) was cooled to 0 °C. Aqueous formaldehyde (37%, 5.25 mL, 70.4 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 4 h, washed with water ( $2 \times 20$  mL), dried ( $\text{MgSO}_4$ ) and concentrated in *vacuo* to leave *triazinane* **1g** (2.09 g, 9.80 mmol, 17%) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.53 (6H, s,  $3 \times \text{CH}_2$ ), 2.85 (3H, hept,  $J = 6.5$  Hz,  $3 \times \text{CH}(\text{CH}_3)_2$ ), 1.06 (18H, d,  $J = 6.5$  Hz,  $3 \times \text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  68.6 ( $3 \times \text{CH}_2$ ), 49.9 ( $3 \times \text{CH}$ ), 20.0 ( $6 \times \text{CH}_3$ ). These data are consistent with those reported previously.<sup>10</sup>



*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.31 (1H, dd,  $J = 11.5$ , 1.5 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.60 (2H, t,  $J = 6.8$  Hz,  $\text{CH}_2$ ), 1.93 (3H, d,  $J = 1.5$  Hz,  $\text{CH}_3\text{C}=\text{}$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  124.1 (CH), 123.6 (CH), 24.4 ( $\text{CH}_3$ ).

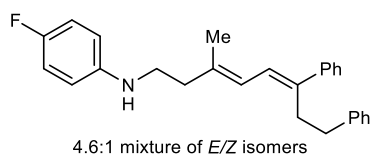


**4-Methoxy-*N*-[(3*Z*,5*Z*)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (**3b**).**

The title compound was prepared according to the general procedure using enyne **1a** (55.3 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol) and PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 5.2:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine 3b* [88.2 mg, 0.22 mmol, 74% (6.0:1 *E:Z*)] as a brown oil. *R*<sub>f</sub> = 2.9 (10% EtOAc/petroleum ether); IR 3395 (N-H), 3025, 2930, 1510 (C=C), 1443, 1234, 1036, 817, 753, 696 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>28</sub>H<sub>32</sub>NO [M+H]<sup>+</sup>: 398.2478, found: 398.2472.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.47 (2H, dd, *J* = 8.3, 1.3 Hz, ArH), 7.40-7.33 (2H, m, ArH), 7.30-7.27 (3H, m, ArH), 7.22-7.14 (3H, m, ArH), 6.81-6.77 (2H, m, ArH), 6.63-6.59 (2H, m, ArH), 6.56 (1H, *J* = 11.3 Hz, HC=CPh), 6.21-6.16 (1H, m, CH<sub>3</sub>C=CH), 3.75 (3H, s, OCH<sub>3</sub>), 3.36 (1H, br s, NH), 3.21 (2H, t, *J* = 6.7 Hz, NCH<sub>2</sub>), 2.96-2.90 (2H, m, CH<sub>2</sub>Ph), 2.74-2.67 (2H, m, CH<sub>2</sub>CH<sub>2</sub>Ph), 2.42 (2H, t, *J* = 6.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 1.85 (3H, d, *J* = 1.3 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.3 (C), 142.9 (C), 142.6 (C), 142.1 (C), 139.3 (C), 137.2 (C), 128.6 (2 × CH), 128.53 (2 × CH), 128.48 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 126.1 (CH), 124.0 (CH), 123.3 (CH), 115.1 (2 × CH), 114.5 (2 × CH), 56.0 (CH<sub>3</sub>), 42.8 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 35.5 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 16.6 (CH<sub>3</sub>).

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.51 (1H, d, *J* = 11.5 Hz, HC=CPh), 6.25 (1H, dd, *J* = 11.5, 1.5 Hz, CH<sub>3</sub>C=CH), 2.54 (2H, t, *J* = 6.8 Hz, CH<sub>2</sub>), 1.88 (3H, d, *J* = 1.5 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 124.2 (CH), 123.7 (CH), 24.5 (CH<sub>3</sub>).



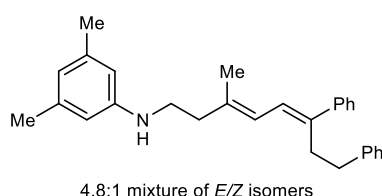
**4-Fluoro-*N*-[(3*Z*,5*Z*)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (**3c**).**

The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1c** (60.8 mg, 0.15 mmol) and PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 3.7:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (10-50% EtOAc/petroleum ether) gave *homoallylic amine 3c* [88.2 mg, 0.22 mmol, 74% (4.6:1 *E:Z*)] as a brown oil. *R*<sub>f</sub> = 0.57 (50% EtOAc/petroleum ether); IR 3405 (N-H), 3026, 2922, 2360, 1596 (C=C), 1509, 1110, 818, 763, 696 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>27</sub>H<sub>28</sub>NF [M+H]<sup>+</sup>: 386.2279, found: 386.2280.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.52-7.46 (2H, m, ArH), 7.42-7.36 (2H, m, ArH), 7.33-7.27 (3H, m, ArH), 7.25-7.21 (1H, m, ArH), 7.20-7.16 (2H, m, ArH), 6.96-6.89 (2H, m, ArH), 6.61-6.55 (3H, m, ArH and HC=CPh), 6.20 (1H, dq, *J* = 11.3, 1.3 Hz, CH<sub>3</sub>C=CH), 3.55

(1H, br s, **NH**), 3.23 (2H, td,  $J = 6.7, 2.0$  Hz, **NCH<sub>2</sub>**), 2.99-2.92 (2H, m, **CH<sub>2</sub>Ph**), 2.77-2.69 (2H, m, **CH<sub>2</sub>CH<sub>2</sub>Ph**), 2.44 (2H, t,  $J = 6.7$  Hz, **NCH<sub>2</sub>CH<sub>2</sub>**), 1.87 (3H, d,  $J = 1.3$  Hz, **CH<sub>3</sub>**); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.9 (d,  $J_{C-F} = 235.0$  Hz, CF), 144.6 (d,  $J_{C-F} = 1.8$  Hz, C), 142.7 (C), 141.9 (C), 139.3 (C), 136.8 (C), 128.5 (2  $\times$  CH), 128.4 (4  $\times$  CH), 127.1 (CH), 126.3 (2  $\times$  CH), 126.0 (CH), 123.8 (CH), 123.3 (CH), 115.7 (d,  $J_{C-F} = 22.5$  Hz, 2  $\times$  CH), 113.8 (d,  $J_{C-F} = 7.3$  Hz, 2  $\times$  CH), 42.3 (CH<sub>2</sub>), 39.8 (CH<sub>2</sub>), 35.3 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 16.5 (CH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -128.1 (s)

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.28 (1H, dd,  $J = 11.5, 1.5$  Hz, **CH<sub>3</sub>C=CH**), 2.55 (2H, t,  $J = 6.7$  Hz, **CH<sub>2</sub>**), 1.90 (3H, d,  $J = 1.5$  Hz, **CH<sub>3</sub>**); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  124.3 (CH), 123.6 (CH), 31.9 (CH<sub>2</sub>), 24.4 (CH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -128.2 (s).



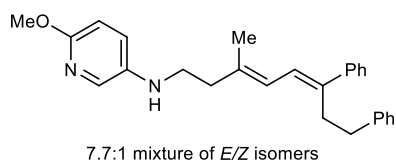
**3,5-Dimethyl-N-[(3Z,5Z)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]aniline (3d).** The title compound was prepared according to the

general procedure on a 0.26 mmol scale, using enyne **2a** (47.9 mg, 0.26 mmol), triazinane **1d** (51.0 mg, 0.13 mmol) and PhB(OH)<sub>2</sub> (47.6 mg, 0.39 mmol) to give the crude product as a 3.6:1 mixture of

inseparable *E/Z* isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave *homoallylic amine 3d* [65.5 mg, 0.17 mmol, 64% (4.8:1 *E:Z*)] as a brown oil.  $R_f = 0.32$  (5% EtOAc/petroleum ether); IR 3401, (N-H), 3025, 2916, 1599 (C=C), 1494, 1445, 1375, 1334, 1303, 1186, 1108, 1078, 1029, 820, 753, 695 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>29</sub>H<sub>33</sub>N [M+H]<sup>+</sup>: 396.2686, found: 396.2674.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50-7.45 (2H, m, **ArH**), 7.41-7.34 (2H, m, **ArH**), 7.32-7.26 (3H, m, **ArH**), 7.23-7.14 (3H, m, **ArH**), 6.57 (1H, d,  $J = 11.3$  Hz, **HC=CPh**), 6.39 (1H, s, **ArH**), 6.29 (2H, d,  $J = 1.5$  Hz, **ArH**), 6.20 (1H, dq,  $J = 11.3, 1.3$  Hz, **CH<sub>3</sub>C=CH**), 3.53 (1H, br s, **NH**), 3.24 (2H, t,  $J = 6.7$  Hz, **NCH<sub>2</sub>**), 2.99-2.91 (2H, m, **CH<sub>2</sub>Ph**), 2.76-2.68 (2H, m, **CH<sub>2</sub>CH<sub>2</sub>Ph**), 2.43 (2H, t,  $J = 6.7$  Hz, **NCH<sub>2</sub>CH<sub>2</sub>**), 2.25 (6H, s, 2  $\times$  **ArCH<sub>3</sub>**), 1.85 (3H, d,  $J = 1.3$  Hz, **CH<sub>3</sub>C=**); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.4 (C), 142.9 (C), 142.1 (C), 139.2 (C), 139.0 (2  $\times$  C), 137.2 (C), 128.6 (CH), 128.54 (3  $\times$  CH), 128.48 (2  $\times$  CH), 127.1 (CH), 126.4 (2  $\times$  CH), 126.1 (CH), 124.0 (CH), 123.3 (CH), 119.6 (CH), 111.0 (2  $\times$  CH), 41.8 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 35.4 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 21.7 (2  $\times$  CH<sub>3</sub>), 16.6 (CH<sub>3</sub>).

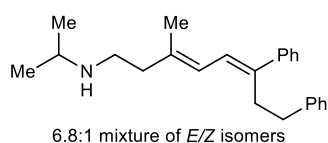
*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.55 (2H, t,  $J = 6.9$  Hz, **CH<sub>2</sub>**), 2.22 (6H, s, 2  $\times$  **ArCH<sub>3</sub>**), 1.89 (3H, d,  $J = 1.3$  Hz, **CH<sub>3</sub>C=**); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  126.3 (CH), 111.0 (CH).



**6-Methoxy-*N*-[(3*Z*,5*Z*)-3-methyl-6,8-diphenylocta-3,5-dien-1-yl]pyridin-3-amine (3e).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1e** (61.3 mg, 0.15 mmol), PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 5.6:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (10-50% EtOAc/petroleum ether) gave *homoallylic amine* **3e** [69.4 mg, 0.17 mmol, 58% (7.7:1 *E:Z*)] as a brown oil. *R*<sub>f</sub> = 0.48 (50% EtOAc/petroleum ether); IR 3271 (N-H), 2926, 2360, 1578 (C=C), 1378, 1261, 1078, 1030, 906, 728, 697 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>27</sub>H<sub>31</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 399.2431, found: 399.2436.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61 (1H, d, *J* = 3.0 Hz, ArH), 7.50-7.46 (2H, m, ArH), 7.40-7.34 (3H, m, ArH), 7.31-7.26 (3H, m, ArH), 7.23-7.15 (3H, m, ArH), 6.99 (1H, dd, *J* = 8.8, 3.0 Hz, ArH), 6.64 (1H, d, *J* = 8.8 Hz, ArH), 6.57 (1H, d, *J* = 11.3 Hz, HC=CPh), 6.17 (1H, dq, *J* = 11.3, 1.3 Hz, CH<sub>3</sub>C=CH), 3.89 (3H, s, OCH<sub>3</sub>), 3.34 (1H, br s, NH), 3.21 (2H, t, *J* = 6.6 Hz, NCH<sub>2</sub>), 2.98-2.90 (2H, m, CH<sub>2</sub>Ph), 2.76-2.67 (2H, m, CH<sub>2</sub>CH<sub>2</sub>Ph), 2.43 (2H, t, *J* = 6.6 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 1.86 (3H, d, *J* = 1.3 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.5 (C), 142.8 (C), 142.0 (C), 139.4 (C), 139.2 (C), 136.7 (C), 130.5 (CH), 128.6 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.1 (CH), 126.4 (2 × CH), 126.1 (CH), 126.0 (CH), 123.8 (CH), 123.4 (CH), 110.9 (CH), 53.4 (CH<sub>3</sub>), 42.6 (CH<sub>2</sub>), 40.0 (CH<sub>2</sub>), 35.4 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 16.6 (CH<sub>3</sub>).

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (1H, d, *J* = 3.0 Hz, ArH), 6.93 (1H, dd, *J* = 8.8, 3.0 Hz, ArH), 6.49 (1H, d, *J* = 11.5 Hz, HC=CPh), 6.27 (1H, dd, *J* = 11.5, 1.5 Hz, CH<sub>3</sub>C=CH), 3.88 (3H, s, OCH<sub>3</sub>), 2.55 (2H, t, *J* = 6.7 Hz, CH<sub>2</sub>), 1.89 (3H, d, *J* = 1.5 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 124.4 (CH), 31.9 (CH<sub>2</sub>), 24.4 (CH<sub>3</sub>).

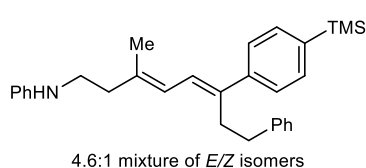


**(3*Z*,5*Z*)-*N*-Isopropyl-3-methyl-6,8-diphenylocta-3,5-dien-1-amine (3g).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1g** (32.0 mg, 0.15 mmol), and PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 5.0:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography using Et<sub>3</sub>N-neutralized silica gel (50% EtOAc/petroleum ether) gave *homoallylic amine* **3g** [58.3 mg, 0.18 mmol, 58% (6.8:1 *E:Z*)] as a dark yellow oil. *R*<sub>f</sub> = 0.45 (50% EtOAc/petroleum ether); *R*<sub>f</sub> = 0.45 (50% EtOAc/petroleum ether); IR 3026, 2962, 1596, 1494, 1444, 1378, 1336, 1173, 1078, 1029, 883, 752, 696 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>24</sub>H<sub>31</sub>N [M+H]<sup>+</sup>: 334.2529, found: 334.2527.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.47-7.44 (2H, m, ArH), 7.36 (2H, t, *J* = 7.7 Hz, ArH), 7.30-7.26 (3H, m, ArH), 7.19 (3H, d, *J* = 7.3 Hz, ArH), 6.56 (1H, d, *J* = 11.4 Hz,

**HC=CPh**), 6.20 (1H, dq,  $J = 11.4, 1.3$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.97-2.89 (2H, m,  $\text{NCH}_2$ ), 2.83 (1H, hept,  $J = 6.3$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), 2.76-2.67 (4H, m,  $\text{CH}_2\text{Ph}$  and  $\text{NCH}_2\text{CH}_2$ ), 2.33 (2H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.83 (3H, d,  $J = 1.3$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 1.08 (6H, d,  $J = 6.3$  Hz,  $(\text{CH}_3)_2\text{CH}$ ), **NH** not observed;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0 (C), 142.1 (C), 138.9 (C), 138.0 (C), 128.54 ( $2 \times \text{CH}$ ), 128.50 ( $2 \times \text{CH}$ ), 128.46 ( $2 \times \text{CH}$ ), 127.0 (CH), 126.4 ( $2 \times \text{CH}$ ), 126.0 (CH), 124.1 (CH), 122.7 (CH), 48.8 (CH), 45.5 ( $\text{CH}_2$ ), 41.0 ( $\text{CH}_2$ ), 35.4 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_2$ ), 23.1 ( $2 \times \text{CH}_3$ ), 16.8 ( $\text{CH}_3$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.31-6.27 (1H, m,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.16 (2H, t,  $J = 7.0$  Hz,  $\text{CH}_2$ ), 1.77 (3H, d,  $J = 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 1.01 (6H, d,  $J = 6.2$  Hz,  $(\text{CH}_3)_2\text{CH}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  123.2 (CH), 40.4 ( $\text{CH}_2$ ), 23.0 ( $\text{CH}_3$ ).

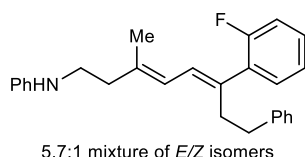


***N*-{(3*Z*,5*Z*)-3-Methyl-8-phenyl-6-[4-(trimethylsilyl)phenyl]octa-3,5-dien-1-yl}aniline (**3h**).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1a** (47.3 mg, 0.15 mmol), and (4-(trimethylsilyl)phenyl)boronic acid (87.3 mg, 0.45 mmol) to give the crude product as a 4.6:1 mixture

of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine 3h* [99.5 mg, 0.27 mmol, 75% (4.6:1 *E:Z*)] as a brown gum.  $R_f = 0.37$  (10% EtOAc/petroleum ether);  $R_f = 0.37$  (10% EtOAc/petroleum ether); IR 3408 (N-H), 3023, 2952, 1601 (C=C), 1495, 1317, 1247, 1178, 1110, 837, 819, 747, 693  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{30}\text{H}_{38}\text{NSi}$   $[\text{M}+\text{H}]^+$ : 440.2768, found: 440.2767.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.53 (2H, d,  $J = 8.2$  Hz, **ArH**), 7.48-7.44 (2H, m, **ArH**), 7.24-7.13 (6H, m, **ArH**), 6.75-6.69 (1H, m, **ArH**), 6.67-6.55 (4H, m,  $\text{CH}_3\text{C}=\text{CHCH}$  and **ArH**), 6.18 (1H, dq,  $J = 11.4, 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.67 (1H, br s, **NH**), 3.25 (2H, t,  $J = 6.7$  Hz,  $\text{NCH}_2$ ), 2.98-2.87 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.77-2.67 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.44 (2H, t,  $J = 6.7$  Hz,  $\text{NCH}_2\text{CH}_2$ ), 1.85 (3H, d,  $J = 1.3$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 0.30 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3 (C), 143.2 (C), 142.1 (C), 139.3 (C), 139.2 (C), 137.2 (C), 133.7 ( $2 \times \text{CH}$ ), 129.4 (CH), 128.6 (CH), 128.5 ( $3 \times \text{CH}$ ), 126.1 (CH), 125.7 ( $2 \times \text{CH}$ ), 124.1 (CH), 123.4 (CH), 117.5 (CH), 113.1 ( $3 \times \text{CH}$ ), 41.8 ( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_2$ ), 16.6 ( $\text{CH}_3$ ), -0.9 ( $3 \times \text{CH}_3$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.26 (1H, d,  $J = 11.5$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.55 (2H, t,  $J = 6.9$  Hz,  $\text{CH}_2$ ), 1.88 (3H, d,  $J = 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 0.27 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  124.2 (CH), 123.7 (CH), 32.1 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_3$ ).

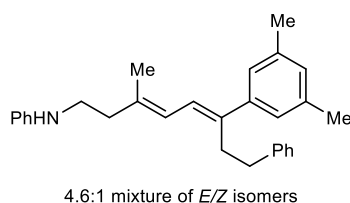


***N*-[*(3Z,5Z)*-6-(2-Fluorophenyl)-3-methyl-8-phenylocta-3,5-dien-1-yl]aniline (3i).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1a** (47.3 mg, 0.15 mmol), and (2-fluorophenyl)boronic acid (63.0 mg, 0.45 mmol) to

give the crude product as a 3.8:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine 3i* [55.6 mg, 0.14 mmol, 48% (5.7:1 *E:Z*)] as a brown oil.  $R_f$  = 0.15 (5% EtOAc/petroleum ether); IR 3406 (N-H), 3025, 2922, 1601, 1504, 1447, 1377, 1315, 1263, 1211, 1179, 1153, 1102, 1072, 1029, 992, 866, 817, 747, 692  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{27}\text{H}_{28}\text{FN}$   $[\text{M}+\text{H}]^+$ : 386.2279, found: 386.2032.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.28 (1H, m, ArH), 7.27-7.24 (2H, m, ArH), 7.23-7.06 (8H, m, ArH), 6.74 (1H, dd,  $J$  = 7.9, 6.7 Hz, ArH), 6.68-6.63 (2H, m, ArH), 6.43 (1H, d,  $J$  = 11.4 Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.22 (1H, dq,  $J$  = 11.4, 1.4 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.65 (1H, br s, NH), 3.27 (2H, t,  $J$  = 6.7 Hz,  $\text{NCH}_2$ ), 2.96-2.90 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.73-2.65 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.45 (2H, t,  $J$  = 6.7 Hz,  $\text{NCH}_2\text{CH}_2$ ), 1.83 (3H, d,  $J$  = 1.4 Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3 (d,  $J_{\text{C-F}}$  = 246.3 Hz, CF), 148.3 (C), 142.0 (C), 137.7 (C), 135.6 (C), 131.5 (d,  $J_{\text{C-F}}$  = 13.7 Hz, C), 130.52 (CH), 130.49 (CH), 129.4 ( $2 \times$  CH), 128.6 ( $2 \times$  CH), 128.4 ( $2 \times$  CH), 127.0 (d,  $J_{\text{C-F}}$  = 2.0 Hz, CH), 126.0 (CH), 124.2 (d,  $J_{\text{C-F}}$  = 3.4 Hz, CH), 122.7 (CH), 117.5 (CH), 115.9 (d,  $J_{\text{C-F}}$  = 22.8 Hz, CH), 113.1 ( $2 \times$  CH), 41.8 ( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 35.1 ( $\text{CH}_2$ ), 33.1 (d,  $J_{\text{C-F}}$  = 2.8 Hz,  $\text{CH}_2$ ), 16.6 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.7 (s).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.63-6.59 (2H, m, ArH), 6.39 (1H, d,  $J$  = 11.5 Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.31-6.27 (1H, m,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.53 (2H, t,  $J$  = 6.9 Hz,  $\text{CH}_2$ ), 1.90 (3H, d,  $J$  = 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  126.6 (CH), 123.5 (CH), 32.0 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.8 (s).

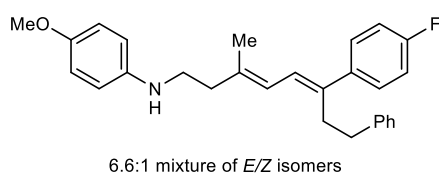


***N*-[*(3Z,5Z)*-6-(3,5-Dimethylphenyl)-3-methyl-8-phenylocta-3,5-dien-1-yl]aniline (3j).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1a** (47.3 mg, 0.15 mmol), and (3,5-dimethylphenyl)boronic acid (67.5

mg, 0.45 mmol) to give the crude product as a 3.0:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine 3j* [82.2 mg, 0.21 mmol, 69% (4.6:1 *E:Z*)] as a pale brown oil.  $R_f$  = 0.14 (5% EtOAc/petroleum ether); IR 3393 (N-H), 3024, 2920, 1601, 1505, 1453, 1375, 1316, 1262, 1178, 1030, 908, 856, 747, 693, 507  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{29}\text{H}_{34}\text{N}$   $[\text{M}+\text{H}]^+$ : 396.2686, found: 396.2688.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.26 (2H, m, ArH), 7.23-7.14 (5H, m, ArH), 7.07 (2H, br s, ArH), 6.94 (1H, s, ArH), 6.75-6.70 (1H, m, ArH), 6.66-6.62 (2H, m, ArH), 6.53 (1H, d,  $J = 11.3$  Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.17 (1H, dq,  $J = 11.3, 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.66 (1H, br s, NH), 3.25 (2H, t,  $J = 6.7$  Hz,  $\text{NCH}_2$ ), 2.96-2.88 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.75-2.67 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.44 (2H, t,  $J = 6.7$  Hz,  $\text{NCH}_2\text{CH}_2$ ), 2.36 (6H, s,  $2 \times \text{ArCH}_3$ ), 1.86 (3H, d,  $J = 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3 (C), 143.0 (C), 142.2 (C), 139.7 (C), 138.0 ( $2 \times \text{C}$ ), 136.7 (C), 129.4 ( $2 \times \text{CH}$ ), 128.9 (CH), 128.6 ( $2 \times \text{CH}$ ), 128.5 ( $2 \times \text{CH}$ ), 126.0 (CH), 124.4 ( $2 \times \text{CH}$ ), 123.6 (CH), 123.4 (CH), 117.5 (CH), 113.1 ( $2 \times \text{CH}$ ), 41.8 ( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_2$ ), 32.4 ( $\text{CH}_2$ ), 21.6 ( $2 \times \text{CH}_3$ ), 16.6 ( $\text{CH}_3$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (2H, d,  $J = 1.5$  Hz, ArH), 6.26 (1H, dd,  $J = 11.6, 1.5$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.56 (2H, t,  $J = 6.9$  Hz,  $\text{CH}_2$ ), 2.34 (6H, s,  $2 \times \text{ArCH}_3$ ), 1.88 (3H, d,  $J = 1.5$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  124.1 (CH), 32.1 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_3$ ), 21.3 ( $2 \times \text{CH}_3$ ).

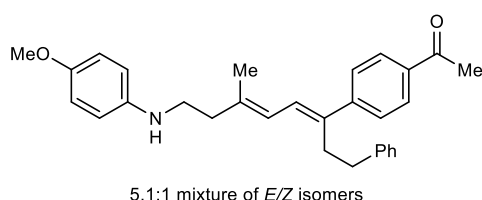


***N*-[*(3E,5E)*-6-(4-Fluorophenyl)-3-methyl-8-phenylocta-3,5-dien-1-yl]-4-methoxyaniline (**3k**).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and

(4-fluorophenyl)boronic acid (63.0 mg, 0.45 mmol) to give the crude product as a 4.7:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine 3k* [105 mg, 0.25 mmol, 84% (6.6:1 *E:Z*)] as a brown oil.  $R_f = 0.24$  (10% EtOAc/petroleum ether); IR 3406 (N-H), 2929, 1600 (C=C), 1504, 1453, 1232, 1036, 816, 749, 698  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{28}\text{H}_{31}\text{FNO}$   $[\text{M}+\text{H}]^+$ : 416.2384, found: 416.2698.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.40 (2H, m, ArH), 7.33-7.26 (2H, m, ArH), 7.25-7.14 (3H, m, ArH), 7.11-7.03 (2H, m, ArH), 6.85-6.78 (2H, m, ArH), 6.66-6.60 (2H, m, ArH), 6.51 (1H, d,  $J = 11.3$  Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.18 (1H, dq,  $J = 11.3, 1.3$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.78 (3H, s,  $\text{OCH}_3$ ), 3.24 (2H, t,  $J = 6.6$  Hz,  $\text{NCH}_2$ ), 2.97-2.89 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.75-2.67 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.45 (2H, t,  $J = 6.6$  Hz,  $\text{NCH}_2\text{CH}_2$ ), 1.87 (3H, d,  $J = 1.3$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), NH not observed;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2 (d,  $J_{\text{C-F}} = 246.0$  Hz, CF), 152.3 (C), 142.6 (C), 141.9 (C), 139.0 (C), 138.2 (C), 137.3 (C), 128.5 ( $5 \times \text{CH}$ ), 127.9 (d,  $J_{\text{C-F}} = 7.8$  Hz,  $2 \times \text{CH}$ ), 126.1 (CH), 123.9 (CH), 123.4 (CH), 115.5 (CH), 115.3 (CH), 115.1 ( $2 \times \text{CH}$ ), 114.5 (CH), 55.9 ( $\text{CH}_3$ ), 42.8 ( $\text{CH}_2$ ), 40.1 ( $\text{CH}_2$ ), 35.3 ( $\text{CH}_2$ ), 32.4 ( $\text{CH}_2$ ), 16.6 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.8 (s).

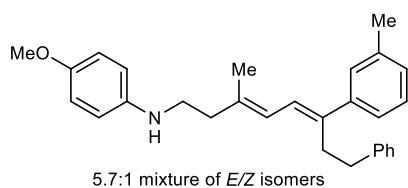
*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.43 (1H, d,  $J = 11.5$  Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.28-6.22 (1H, m,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.55 (2H, t,  $J = 6.7$  Hz,  $\text{CH}_2$ ), 1.90 (3H, d,  $J = 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  124.1 (CH), 123.7 (CH), 32.0 ( $\text{CH}_2$ ), 25.8 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.9 (s).



**1-(4-[(3*E*,5*E*)-8-[(4-Methoxyphenyl)amino]-6-methyl-1-phenylocta-3,5-dien-3-yl]phenyl)ethan-1-one (3l).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and (4-acetylphenyl)boronic acid (73.8 mg, 0.45 mmol) to give the crude product as a 4.2:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-30% EtOAc/petroleum ether) gave *homoallylic amine* **3l** [92.8 mg, 0.21 mmol, 70% (5.1:1 *E:Z*)] as a brown oil.  $R_f = 0.27$  (30% EtOAc/petroleum ether); IR 3392 (N-H), 2929, 1677 (C=O), 1598, 1511, 1357, 1236, 956, 819, 750  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{30}\text{H}_{33}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 440.2584, found: 440.2578.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97-7.92 (2H, m, ArH), 7.58-7.51 (2H, m, ArH), 7.31-7.25 (2H, m, ArH), 7.22-7.17 (1H, m, ArH), 7.17-7.12 (2H, m, ArH), 6.83-6.74 (2H, m, ArH), 6.68 (1H, d,  $J = 11.3$  Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.61 (2H, d,  $J = 8.9$  Hz, ArH), 6.23-6.16 (1H, m,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.75 (3H, s,  $\text{OCH}_3$ ), 3.22 (2H, t,  $J = 6.7$  Hz,  $\text{NCH}_2$ ), 2.94 (2H, dd,  $J = 9.7, 6.4$  Hz,  $\text{CH}_2\text{Ph}$ ), 2.73-2.67 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.62 (3H, s,  $\text{CH}_3\text{C}=\text{O}$ ), 2.44 (2H, t,  $J = 6.7$  Hz,  $\text{NCH}_2\text{CH}_2$ ), 1.88 (3H, d,  $J = 1.3$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), NH not observed;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8 (C), 152.3 (C), 147.6 (C), 142.4 (C), 141.6 (C), 139.2 (C), 138.0 (C), 135.6 (C), 128.8 (2  $\times$  CH), 128.5 (2  $\times$  CH), 128.5 (2  $\times$  CH), 126.3 (2  $\times$  CH), 126.2 (CH), 125.8 (CH), 123.1 (CH), 115.1 (2  $\times$  CH), 114.5 (2  $\times$  CH), 55.9 ( $\text{CH}_3$ ), 42.8 ( $\text{CH}_2$ ), 40.2 ( $\text{CH}_2$ ), 35.4 ( $\text{CH}_2$ ), 31.9 ( $\text{CH}_2$ ), 26.7 ( $\text{CH}_3$ ), 16.8 ( $\text{CH}_3$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (2H, d,  $J = 8.0$  Hz, ArH), 7.38-7.33 (2H, m, ArH), 6.28-6.24 (1H, m,  $\text{CH}_3\text{C}=\text{CH}$ ), 1.90 (3H, d,  $J = 1.4$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  127.2 (CH), 124.1 (CH), 24.5 ( $\text{CH}_3$ ).



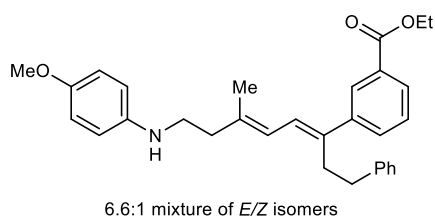
**4-Methoxy-N-[(3*E*,5*E*)-3-methyl-8-phenyl-6-(*m*-tolyl)octa-3,5-dien-1-yl]aniline (3m).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and *m*-tolylboronic acid (61.2 mg, 0.45 mmol) to give the crude product as a 4.8:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave



*homoallylic amine 3m* [103.3 mg, 0.25 mmol, 83% (5.7:1 *E:Z*)] as a brown oil.  $R_f$  = 0.28 (10% EtOAc/petroleum ether); IR 3390 (N-H), 2925, 1601 (C=O), 1510, 1453, 1235, 1178, 1037, 878, 784, 750, 698  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{29}\text{H}_{33}\text{NO}$   $[\text{M}+\text{H}]^+$ : 412.2635, found: 412.2630.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.26 (5H, m, ArH), 7.25-7.04 (4H, m, ArH), 6.79 (2H, d,  $J$  = 8.9 Hz, ArH), 6.63-6.57 (2H, m, ArH), 6.57-6.51 (1H, m,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.17 (1H, dq,  $J$  = 11.4, 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.75 (3H, s,  $\text{OCH}_3$ ), 3.21 (2H, t,  $J$  = 6.6 Hz,  $\text{NCH}_2$ ), 2.96-2.88 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.74-2.67 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.44 (2H, t,  $\text{NCH}_2\text{CH}_2$ ), 2.42 (3H, s,  $\text{ArCH}_3$ ), 1.85 (3H, d,  $J$  = 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), NH not observed;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3 (C), 142.9 (C), 142.6 (C), 142.1 (C), 139.5 (C), 138.1 (C), 137.0 (C), 128.6 ( $2 \times \text{CH}$ ), 128.48 ( $2 \times \text{CH}$ ), 128.46 (CH), 127.9 (CH), 127.2 (CH), 126.0 (CH), 123.8 (CH), 123.6 (CH), 123.4 (CH), 115.1 ( $2 \times \text{CH}$ ), 114.5 ( $2 \times \text{CH}$ ), 56.0 ( $\text{CH}_3$ ), 42.8 ( $\text{CH}_2$ ), 40.1 ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_2$ ), 32.3 ( $\text{CH}_2$ ), 21.8 ( $\text{CH}_3$ ), 16.6 ( $\text{CH}_3$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.77 (2H, d,  $J$  = 8.8 Hz, ArH), 6.53 (1H, d,  $J$  = 11.5 Hz,  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.27 (1H, d,  $J$  = 11.5 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.75 (3H, s,  $\text{OCH}_3$ ), 2.56 (2H, t,  $J$  = 7.0 Hz,  $\text{CH}_2$ ), 1.90 (3H, s,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  124.2 (CH), 55.9 ( $\text{CH}_3$ ), 32.0 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_3$ ).



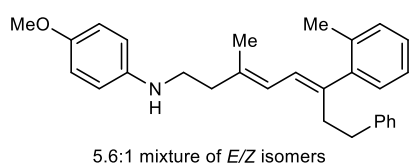
**Ethyl 3-{[3*E*,5*E*]-8-[(4-methoxyphenyl)amino]-6-methyl-1-phenylocta-3,5-dien-3-yl}benzoate (3n).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and [3-(ethoxycarbonyl)phenyl]boronic acid (87.3 mg, 0.45 mmol) to

give the crude product as a 4.5:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (10-30% EtOAc/petroleum ether) gave *homoallylic amine 3n* [92.1 mg, 0.20 mmol, 65% (6.6:1 *E:Z*)] as a brown oil.  $R_f$  = 0.33 (10% EtOAc/petroleum ether); IR 3385 (N-H), 2932, 1715 (C=O), 1601 (C=C), 1510, 1453, 1367, 1285, 1234, 1179, 1108, 1034, 818, 755, 698  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{31}\text{H}_{36}\text{NO}_3$   $[\text{M}+\text{H}]^+$ : 470.2690, found: 470.2698.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (1H, t,  $J$  = 1.8 Hz, ArH), 7.95 (1H, dt,  $J$  = 7.9, 1.4 Hz, ArH), 7.63 (1H, dt,  $J$  = 7.9, 1.4 Hz, ArH), 7.43 (1H, t,  $J$  = 7.9 Hz, ArH), 7.28-7.24 (3H, m, ArH), 7.18-7.13 (2H, m, ArH), 6.80 (2H, d,  $J$  = 8.9 Hz, ArH), 6.64-6.56 (3H, m, ArH and  $\text{CH}_3\text{C}=\text{CHCH}$ ), 6.19 (1H, dq,  $J$  = 11.3, 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 4.42 (2H, q,  $J$  = 7.1 Hz,  $\text{CH}_2\text{CH}_3$ ), 3.75 (3H, s,  $\text{OCH}_3$ ), 3.22 (2H, t,  $J$  = 6.7 Hz,  $\text{NCH}_2$ ), 2.98-2.92 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.73-2.67 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.44 (2H, t,  $J$  = 6.7 Hz,  $\text{NCH}_2\text{CH}_2$ ), 1.87 (3H, d,  $J$  = 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 1.43 (3H, t,  $J$  = 7.1 Hz,  $\text{CH}_2\text{CH}_3$ ), NH not observed;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9 (C), 152.3 (C), 143.2 (C),

142.5 (C), 141.8 (C), 138.3 (C), 138.1 (C), 130.8 (C), 130.7 (CH), 128.6 (CH), 128.53 (2 × CH), 128.5 (2 × CH), 128.1 (CH), 127.5 (CH), 126.1 (CH), 124.8 (CH), 123.1 (CH), 115.1 (2 × CH), 114.5 (2 × CH), 61.2 (CH<sub>2</sub>), 56.0 (CH<sub>3</sub>), 42.8 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 35.3 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 16.8 (CH<sub>3</sub>), 14.5 (CH<sub>3</sub>).

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.73 (2H, d, *J* = 8.9 Hz, ArH), 6.56 (2H, d, *J* = 8.9 Hz, ArH), 6.52 (1H, d, *J* = 11.5 Hz, CH<sub>3</sub>C=CHCH), 6.26 (1H, dd, *J* = 11.5, 1.5 Hz, CH<sub>3</sub>C=CH), 2.55 (2H, t, *J* = 6.9 Hz, CH<sub>2</sub>), 1.89 (3H, d, *J* = 1.5 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 115.0 (CH), 114.3 (CH), 32.2 (CH<sub>2</sub>), 24.5 (CH<sub>3</sub>).

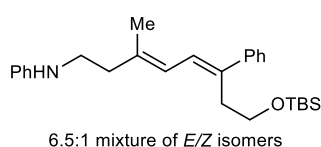


**4-Methoxy-*N*-[(3*E*,5*E*)-3-methyl-8-phenyl-6-(*o*-tolyl)octa-3,5-dien-1-yl]aniline (3o).** The title compound was prepared according to the general procedure using enyne **2a** (55.3 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and *o*-tolylboronic acid (61.2

mg, 0.45 mmol) to give the crude product as a 2.5:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine* **3o** [20 mg, 0.05 mmol, 16% (5.6:1 *E:Z*)] as a brown oil. *R*<sub>f</sub> = 0.30 (10% EtOAc/petroleum ether); IR 3312 (N-H), 2919, 1602 (C=C), 1510, 1453, 1236, 1035, 817, 752, 730, 698 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>29</sub>H<sub>33</sub>NO [M+H]<sup>+</sup>: 412.2635, found: 412.2634.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 -7.10 (9H, m, ArH), 6.79 (2H, d, *J* = 8.9 Hz, ArH), 6.62 (2H, d, *J* = 8.9 Hz, ArH), 6.23 (1H, dq, *J* = 11.3, 1.3 Hz, CH<sub>3</sub>C=CH), 6.14 (1H, d, *J* = 11.3 Hz, CH<sub>3</sub>C=CHCH), 3.75 (3H, s, OCH<sub>3</sub>), 3.40 (1H, br s, NH), 3.22 (2H, t, *J* = 6.7 Hz, NCH<sub>2</sub>), 2.83-2.75 (2H, m, PhCH<sub>2</sub>), 2.66-2.58 (2H, m, CH<sub>2</sub>CH<sub>2</sub>Ph), 2.43 (2H, t, *J* = 6.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.30 (3H, s, ArCH<sub>3</sub>), 1.78 (3H, d, *J* = 1.3 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.3 (C), 144.2 (C), 142.6 (C), 142.1 (C), 140.7 (C), 136.3 (C), 135.5 (C), 130.4 (CH), 129.1 (4 × CH), 128.5 (CH), 126.9 (CH), 126.0 (CH), 125.6 (CH), 125.4 (CH), 122.7 (CH), 115.1 (2 × CH), 114.5 (2 × CH), 56.0 (CH<sub>3</sub>), 42.9 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 34.8 (CH<sub>2</sub>), 34.4 (CH<sub>2</sub>), 20.4 (CH<sub>3</sub>), 16.5 (CH<sub>3</sub>).

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.73 (2H, d, *J* = 8.8 Hz, ArH), 6.53 (2H, d, *J* = 8.8 Hz, ArH), 6.30 (1H, d, *J* = 12.1 Hz, CH<sub>3</sub>C=CH), 3.73 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 115.0 (CH), 114.3 (CH).

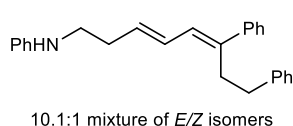


***N*-[(3*Z*,5*Z*)-8-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-6-phenylocta-3,5-dien-1-yl]aniline (3p).** The title compound was prepared according to the general procedure using enyne **2b** (71.5 mg, 0.30 mmol), triazinane **1b** (47.3 mg, 0.15 mmol), and PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 3.1:1

mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (10% EtOAc/petroleum ether) gave *homoallylic amine 3p* [49.0 mg, 0.12 mmol, 39% (6.5:1 *E:Z*)] as a brown oil. Data for major isomer:  $R_f$  = 0.47 (10% EtOAc/petroleum ether); IR 3405 (N-H), 3051, 2953, 2927, 2855, 1601 (C=C), 1505, 1360, 1095, 834, 774, 747, 692  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{27}\text{H}_{40}\text{NOSi}$   $[\text{M}+\text{H}]^+$ : 422.2874, found: 422.2876.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.45 (2H, m, ArH), 7.39-7.33 (3H, m, ArH), 7.25-7.18 (2H, m, ArH), 6.75-6.69 (1H, m, ArH), 6.69-6.60 (3H, m,  $\text{HC}=\text{CPh}$  and ArH), 6.35 (1H, dq,  $J$  = 11.3, 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.74-3.62 (2H, m,  $\text{CH}_2\text{O}$ ), 3.30 (2H, t,  $J$  = 6.8 Hz,  $\text{NCH}_2$ ), 2.93 (2H, t,  $J$  = 7.4 Hz,  $\text{CH}_2\text{CH}_2\text{O}$ ), 2.50 (2H, t,  $J$  = 6.8 Hz,  $\text{NCH}_2\text{CH}_2$ ), 1.90 (3H, d,  $J$  = 1.3 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 0.90 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.04 (6H, s,  $\text{Si}(\text{CH}_3)_2$ ), NH not observed;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3 (C), 137.2 (C), 137.2 (C), 136.5 (C), 129.4 (2  $\times$  CH), 128.5 (2  $\times$  CH), 127.1 (CH), 126.4 (2  $\times$  CH), 125.0 (CH), 123.8 (CH), 117.6 (CH), 113.0 (2  $\times$  CH), 62.5 ( $\text{CH}_2$ ), 41.9 ( $\text{CH}_2$ ), 40.2 ( $\text{CH}_2$ ), 34.0 ( $\text{CH}_2$ ), 26.1 (3  $\times$   $\text{CH}_3$ ), 18.5 (C), 16.6 ( $\text{CH}_3$ ), -5.12 (2  $\times$   $\text{CH}_3$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.40 (1H, app d,  $J$  = 11.7 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.58 (2H, t,  $J$  = 6.9 Hz,  $\text{CH}_2$ ), 1.93 (3H, d,  $J$  = 1.4 Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 0.89 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.03 (6H, s, 2  $\times$   $\text{CH}_3$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  124.7 (CH), 32.1 ( $\text{CH}_2$ ), 24.4 ( $\text{CH}_3$ ).

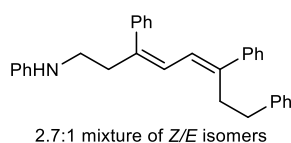


***N*-[*(3Z,5Z)*-6,8-Diphenylocta-3,5-dien-1-yl]aniline (3q).** The title compound was prepared according to the general procedure using enyne **2c** (51.0 mg, 0.30 mmol), triazinane **1a** (47.3 mg, 0.15 mmol), and  $\text{PhB}(\text{OH})_2$  (54.9 mg, 0.45 mmol) to give the crude product as a 3.3:1 mixture of inseparable *E/Z* isomers.

Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave *homoallylic amine 3q* [38.4 mg, 0.11 mmol, 36% (10.1:1 *E:Z*)] as a brown oil.  $R_f$  = 0.27 (5% EtOAc/petroleum ether); IR 3405 (N-H), 3053, 3023, 2922, 2857, 1601 (C=C), 1504, 1317, 963, 748, 693  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{26}\text{H}_{28}\text{N}$   $[\text{M}+\text{H}]^+$ : 354.2216, found: 354.2209.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.44 (2H, m, ArH), 7.39-7.35 (2H, m, ArH), 7.29 (3H, td,  $J$  = 7.3, 5.3 Hz, ArH), 7.23-7.16 (5H, m, ArH), 6.73 (1H, tt,  $J$  = 7.3, 1.1 Hz, ArH), 6.66-6.62 (2H, m, ArH), 6.43-6.35 (2H, m,  $\text{HC}=\text{CPh}$  and  $\text{NCH}_2\text{CH}_2\text{CH}=\text{CH}$ ), 5.78 (1H, dt,  $J$  = 13.8, 7.4 Hz,  $\text{CH}_2\text{CH}=\text{CH}$ ), 3.67 (1H, br s, NH), 3.21 (2H, t,  $J$  = 6.7 Hz,  $\text{NCH}_2$ ), 2.98-2.91 (2H, m,  $\text{CH}_2\text{Ph}$ ), 2.74-2.69 (2H, m,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.46 (2H, q,  $J$  = 6.7 Hz,  $\text{NCH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3 (C), 142.2 (C), 141.9 (C), 139.3 (C), 132.4 (CH), 129.4 (2  $\times$  CH), 129.1 (CH), 128.6 (4  $\times$  CH), 128.5 (2  $\times$  CH), 127.8 (CH), 127.2 (CH), 126.4 (2  $\times$  CH), 126.1 (CH), 117.6 (CH), 113.1 (2  $\times$  CH), 43.5 ( $\text{CH}_2$ ), 35.4 ( $\text{CH}_2$ ), 33.0 ( $\text{CH}_2$ ), 32.2 ( $\text{CH}_2$ ).

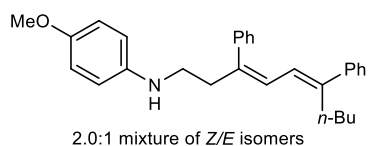
*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.59-5.51 (1H, m,  $\text{CH}_2\text{CH}=\text{CH}$ ), 2.62-2.56 (2H, m,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  27.7 ( $\text{CH}_2$ ).



***N*-[*(3Z,5E)*-3,6,8-Triphenylocta-3,5-dien-1-yl]aniline (3r).** The title compound was prepared according to the general procedure using enyne **2d** (73.9 mg, 0.30 mmol), triazinane **1a** (47.3 mg, 0.15 mmol), and  $\text{PhB(OH)}_2$  (54.9 mg, 0.45 mmol) to give the crude product as a 2.6:1 mixture of inseparable *Z/E* isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave *homoallylic amine 3r* [93.6 mg, 0.22 mmol, 73% (2.7:1 *Z:E*)] as a brown oil. IR 3407 (N-H), 3023, 2928, 1600 ( $\text{C}=\text{C}$ ), 1504, 1452, 1319, 876, 746, 692  $\text{cm}^{-1}$ ;  $R_f$  = 0.27 (5% EtOAc/petroleum ether); HRMS (ESI) Exact mass calculated for  $\text{C}_{32}\text{H}_{32}\text{N}$   $[\text{M}+\text{H}]^+$ : 430.2529, found: 430.2532. Exact mass calculated for  $\text{C}_{32}\text{H}_{31}\text{NNa}$   $[\text{M}+\text{Na}]^+$ : 452.2349, found: 452.2347.

*NMR data of major E-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.28 (13H, m,  $\text{ArH}$ ), 7.27-7.14 (6H, m,  $\text{ArH}$ ), 6.77-6.67 (2H, m,  $\text{HC}=\text{CCH}_2\text{CH}_2\text{Ph}$  and  $\text{ArH}$ ), 6.59 (1H, dt,  $J$  = 8.8, 1.8 Hz,  $\text{NCH}_2\text{CH}_2\text{C}=\text{CH}$ ), 3.68 (1H, br s,  $\text{NH}$ ), 3.24 (1H, t,  $J$  = 6.8 Hz,  $\text{NCH}_2$ ), 3.09-2.98 (4H, m,  $\text{CH}_2\text{Ph}$  and  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 2.78 (2H, dd,  $J$  = 8.6, 6.8 Hz,  $\text{NCH}_2\text{CH}_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0 (C), 142.4 ( $2 \times \text{C}$ ), 142.1 (C), 141.9 (C), 139.3 (C), 129.4 ( $2 \times \text{CH}$ ), 128.7 (CH), 128.66 ( $2 \times \text{CH}$ ), 128.65 ( $2 \times \text{CH}$ ), 128.5 ( $3 \times \text{CH}$ ), 127.5 (CH), 127.4 (CH), 126.5 ( $4 \times \text{CH}$ ), 126.1 (CH), 125.8 (CH), 124.2 (CH), 117.5 (CH), 113.0 ( $2 \times \text{CH}$ ), 42.7 ( $\text{CH}_2$ ), 35.3 ( $\text{CH}_2$ ), 32.1 ( $\text{CH}_2$ ), 29.8 ( $\text{CH}_2$ ).

*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.42 (1H, d,  $J$  = 3.5 Hz,  $=\text{CH}$ ), 3.15 (2H, t,  $J$  = 6.8 Hz,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  113.1 (CH), 42.5 ( $\text{CH}_2$ ), 39.2 ( $\text{CH}_2$ ).

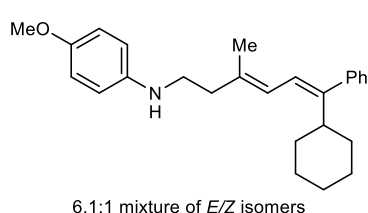


***N*-[*(3Z,5E)*-3,6-Diphenyldeca-3,5-dien-1-yl]-4-methoxyaniline (3s).** The title compound was prepared according to the general procedure using enyne **2h** (59.5 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and  $\text{PhB(OH)}_2$  (54.9 mg, 0.45 mmol) to give the crude product as a 1.2:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5% EtOAc/petroleum ether) gave *homoallylic amine 3s* [88.3 mg, 0.22 mmol, 72% (2.0:1 *E:Z*)] as a brown oil.  $R_f$  = 0.18 (10% EtOAc/petroleum ether); IR 3390 (N-H), 2928, 2857, 1594 ( $\text{C}=\text{C}$ ), 1510, 1440, 1234, 1178, 1034, 817, 758, 696  $\text{cm}^{-1}$ ; HRMS (ESI) Exact mass calculated for  $\text{C}_{29}\text{H}_{34}\text{NO}$   $[\text{M}+\text{H}]^+$ : 412.2635, found: 412.2628.

*NMR data of major Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.47 (2H, m,  $\text{ArH}$ ), 7.41-7.27 (8H, m,  $\text{ArH}$ ), 6.86 (1H, d,  $J$  = 11.5 Hz,  $\text{PhC}=\text{CH}$ ), 6.75-6.71 (2H, m,  $\text{ArH}$ ), 6.67 (d,  $J$  = 11.5 Hz,

PhC=CH), 6.56-6.52 (2H, m, ArH), 3.73 (3H, s, OCH<sub>3</sub>), 3.22 (2H, t,  $J = 7.0$  Hz, NCH<sub>2</sub>), 3.03 (2H, t,  $J = 7.0$  Hz, NCH<sub>2</sub>CH<sub>2</sub>), 2.77-2.70 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.49-1.34 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91 (3H, t,  $J = 7.2$  Hz, CH<sub>2</sub>CH<sub>3</sub>), NH not observed; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.2 (C), 143.8 (C), 142.9 (C), 142.6 (C), 142.2 (C), 139.0 (C), 128.7 (2  $\times$  CH), 128.5 (2  $\times$  CH), 127.4 (CH), 127.3 (CH), 126.4 (2  $\times$  CH), 126.4 (2  $\times$  CH), 125.9 (CH), 123.5 (CH), 115.0 (2  $\times$  CH), 114.4 (2  $\times$  CH), 55.9 (CH<sub>3</sub>), 43.8 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 30.0 (2  $\times$  CH<sub>2</sub>), 22.9 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).

*Characteristic NMR data of minor E-isomer:* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.37 (1H, d,  $J = 11.3$  Hz, =CH), 3.75 (3H, s, OCH<sub>3</sub>), 3.12 (2H, t,  $J = 6.7$  Hz, NCH<sub>2</sub>), 2.83 (2H, t,  $J = 6.7$  Hz, NCH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  124.2 (CH), 41.0 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 20.9 (CH<sub>3</sub>).

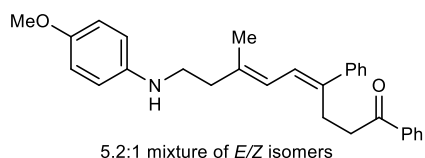


***N*-[*(3E,5E)*-6-Cyclohexyl-3-methyl-6-phenylhexa-3,5-dien-1-yl]-4-methoxyaniline (**3t**).**

The title compound was prepared according to the general procedure using enyne **2e** (48.7 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 4.8:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (5-10% EtOAc/petroleum ether) gave *homoallylic amine 3t* [57.1 mg, 0.15 mmol, 51% (6.1:1 *E:Z*)] as a brown oil.  $R_f = 0.14$  (5% EtOAc/petroleum ether); IR 3398 (N-H), 2925, 2851, 1593 (C=C), 1510, 1441, 1236, 1178, 1117, 1037, 908, 892, 817, 757, 732, 701 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>26</sub>H<sub>34</sub>NO [M+H]<sup>+</sup>: 376.2635, found: 376.2632.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37-7.25 (3H, m, ArH), 7.24-7.19 (2H, m, ArH), 6.83-6.78 (2H, m, ArH), 6.65-6.60 (2H, m, ArH), 6.33 (1H, dq,  $J = 11.5, 1.3$  Hz, CH<sub>3</sub>C=CH), 6.10 (1H, d,  $J = 11.5$  Hz, HC=CPh), 3.76 (3H, s, OCH<sub>3</sub>), 3.23 (2H, t,  $J = 6.6$  Hz, NCH<sub>2</sub>), 2.84-2.72 (1H, m, CH), 2.49-2.42 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>), 1.80-1.62 (9H, m, CH<sub>3</sub>C= and 3  $\times$  CH<sub>2</sub>), 1.40-1.28 (4H, m, 2  $\times$  CH<sub>2</sub>), NH not observed; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.3 (C), 147.0 (C), 144.2 (C), 142.6 (C), 136.1 (C), 128.5 (2  $\times$  CH), 127.7 (2  $\times$  CH), 126.5 (CH), 124.0 (CH), 122.7 (CH), 115.1 (2  $\times$  CH), 114.6 (2  $\times$  CH), 56.0 (CH<sub>3</sub>), 42.8 (CH<sub>2</sub>), 40.9 (CH), 40.1 (CH<sub>2</sub>), 32.3 (2  $\times$  CH<sub>2</sub>), 26.9 (2  $\times$  CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 16.3 (CH<sub>3</sub>).

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.43-6.38 (1H, m, HC=CPh), 6.27 (1H, app d,  $J = 11.6$  Hz, CH<sub>3</sub>C=CH), 3.18 (2H, td,  $J = 6.8, 3.0$  Hz, NCH<sub>2</sub>), 1.91 (3H, d,  $J = 1.4$  Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  123.8 (CH), 123.2 (CH), 50.9 (CH<sub>2</sub>), 24.5 (CH<sub>3</sub>).

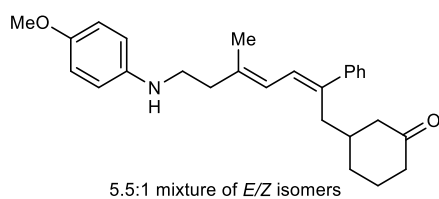


**(4*E*,6*E*)-9-[(4-Methoxyphenyl)amino]-7-methyl-1,4-diphenylnona-4,6-dien-1-one (3u).** The title compound was prepared according to the general procedure using enyne **2f** (63.7 mg, 0.30 mmol), triazinane **1b** (60.8 mg, 0.15 mmol), and

PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 4.1:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (10-30% EtOAc/petroleum ether) gave *homoallylic amine* **3u** [89.1mg, 0.21 mmol, 70% (5.2:1 *E:Z*)] as a brown oil. *R*<sub>f</sub> = 0.23 (10% EtOAc/petroleum ether); IR 3394 (N-H), 3053, 2906, 1681 (C=O), 1600 (C=C), 1505, 1203, 979, 867, 748, 691 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>29</sub>H<sub>32</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 426.2428, found: 426.2427.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93-7.87 (2H, m, ArH), 7.56-7.51 (1H, m, ArH), 7.47-7.26 (7H, m, ArH), 6.79-6.73 (2H, m, ArH), 6.64-6.54 (3H, m, CH<sub>3</sub>C=CH and ArH), 6.33 (1H, dq, *J* = 11.4, 1.3 Hz, HC=CPh), 3.73 (3H, s, OCH<sub>3</sub>), 3.22 (2H, t, *J* = 6.7 Hz, NCH<sub>2</sub>), 3.13-3.02 (4H, m, CH<sub>2</sub>CH<sub>2</sub>C=O), 2.45 (2H, t, *J* = 6.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 1.88 (3H, d, *J* = 1.3 Hz, CH<sub>3</sub>C=), NH not observed; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 199.7 (C), 152.2 (C), 142.6 (C), 142.3 (C), 138.6 (C), 137.8 (C), 136.9 (C), 133.2 (CH), 128.7 (4 × CH), 128.2 (2 × CH), 127.3 (CH), 126.4 (2 × CH), 124.3 (CH), 123.3 (CH), 115.0 (2 × CH), 114.4 (2 × CH), 55.9 (CH<sub>3</sub>), 42.9 (CH<sub>2</sub>), 40.3 (CH<sub>2</sub>), 37.9 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 16.6 (CH<sub>3</sub>).

*Characteristic NMR data of minor Z-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.40-6.35 (1H, m, CH<sub>3</sub>C=CH), 2.56 (2H, t, *J* = 6.8 Hz, CH<sub>2</sub>), 1.91 (3H, d, *J* = 1.3 Hz, CH<sub>3</sub>C=); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 124.0 (CH), 32.2 (CH<sub>2</sub>), 24.5 (CH<sub>3</sub>).



**3-{[2*E*,4*E*]-7-[(4-Methoxyphenyl)amino]-5-methyl-2-phenylhepta-2,4-dien-1-yl}cyclohexan-1-one (3v).** The title compound was prepared according to the general procedure using enyne **2i** (52.9 mg, 0.30 mmol), triazinane **1b** (60.8 mg,

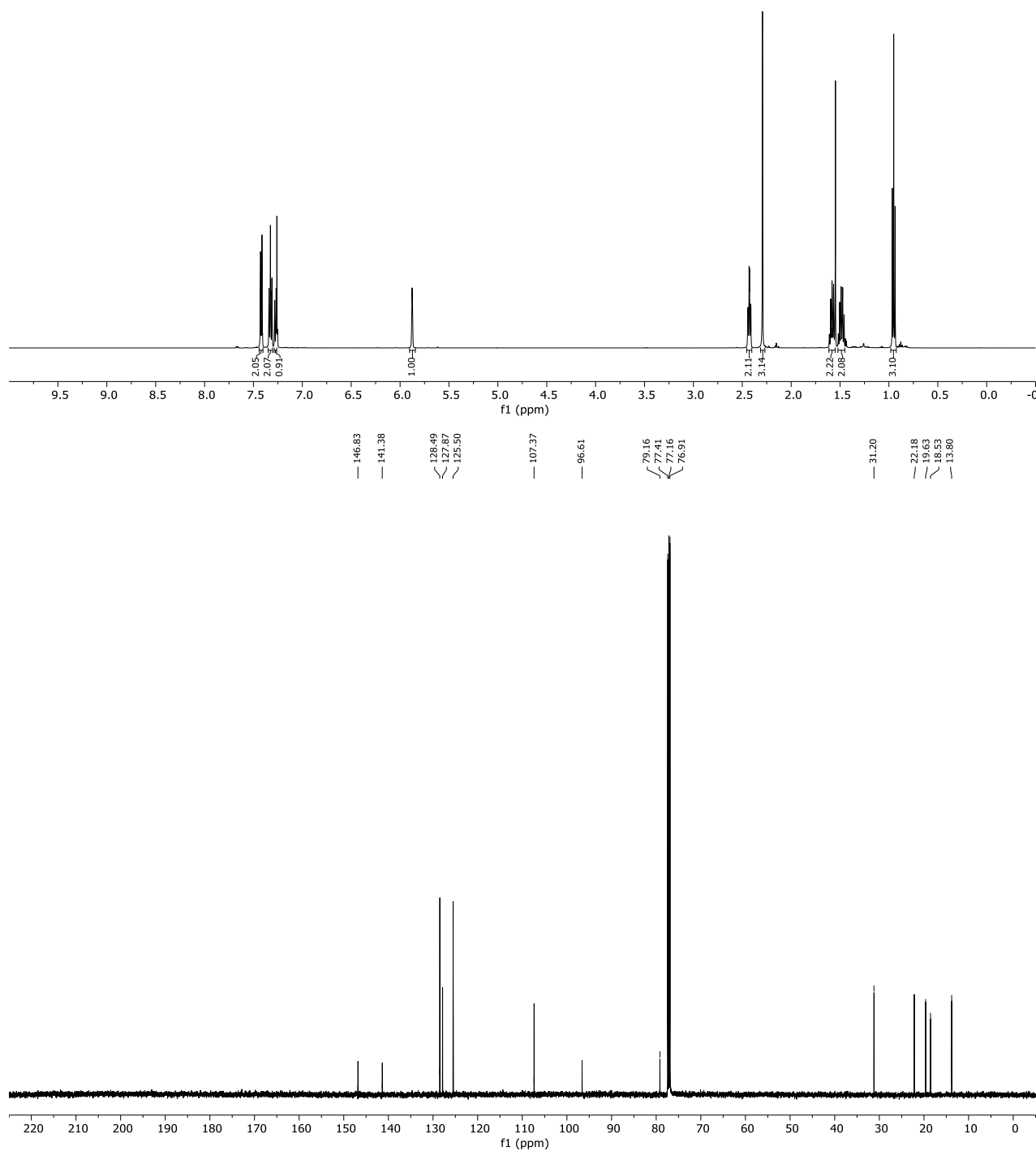
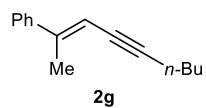
0.15 mmol), and PhB(OH)<sub>2</sub> (54.9 mg, 0.45 mmol) to give the crude product as a 3.2:1 mixture of inseparable *E/Z* isomers. Purification of the residue by column chromatography (10-30% EtOAc/petroleum ether) gave *homoallylic amine* **3v** [72.1 mg, 0.18 mmol, 60% (5.5:1 *E:Z*)] as a dark yellow oil. *R*<sub>f</sub> = 0.28 (30% EtOAc/petroleum ether); IR 3372 (N-H), 2930, 1707 (C=O), 1511, 1235, 1036, 819, 750, 699 cm<sup>-1</sup>; HRMS (ESI) Exact mass calculated for C<sub>27</sub>H<sub>34</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 404.2577, found: 404.2584.

*NMR data of major E-isomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.28 (4H, m, ArH), 7.27-7.23 (1H, m, ArH), 6.82-6.77 (2H, m, ArH), 6.63-6.56 (3H, m, ArH and HC=CPh), 6.22 (1H, dq, *J* = 11.4, 1.3

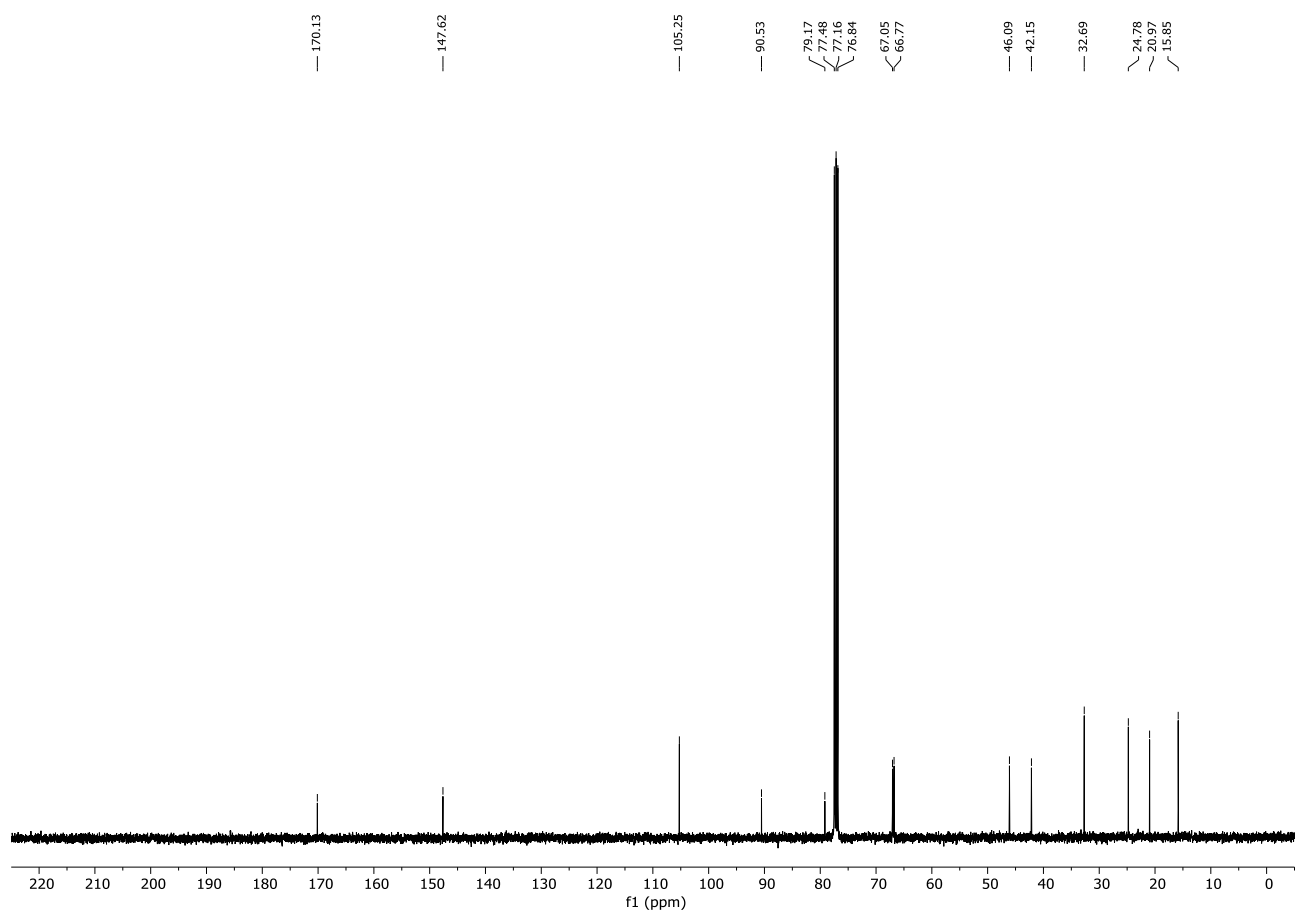
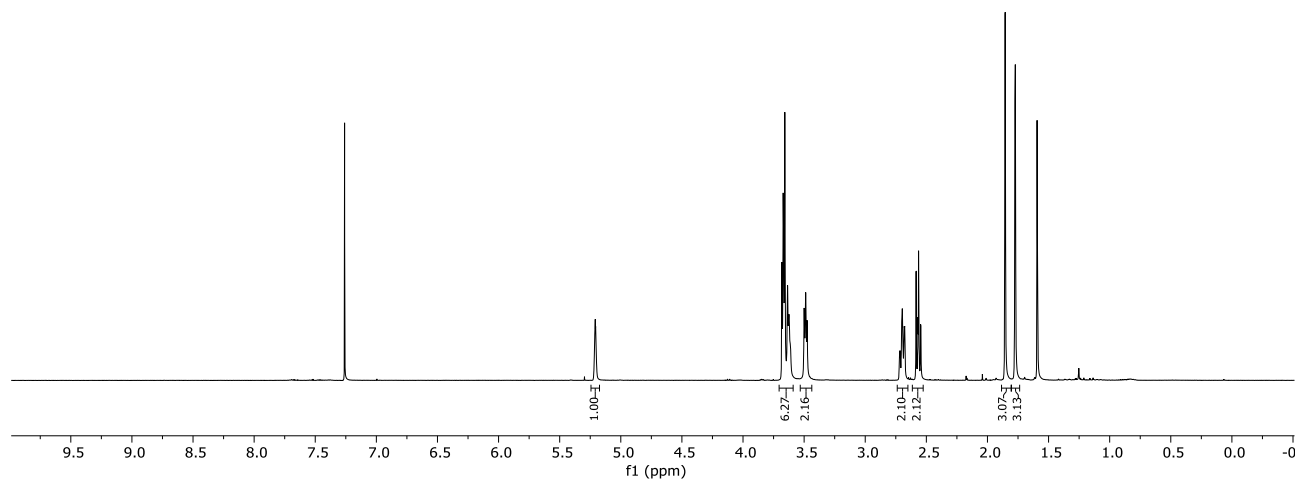
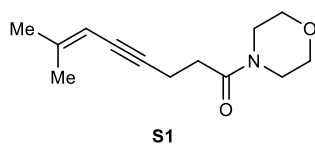
Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 3.75 (3H, s,  $\text{OCH}_3$ ), 3.23 (2H, t,  $J = 6.6$  Hz,  $\text{NCH}_2$ ), 2.67 (2H, dd,  $J = 11.2, 6.7$  Hz,  $=\text{C}(\text{Ph})\text{CH}_2$ ), 2.46 (2H, t,  $J = 6.6$  Hz,  $\text{NCH}_2\text{CH}_2$ ), 2.40-2.31 (1H, m,  $\text{CH}_2\text{C}=\text{O}$ ), 2.33-2.26 (1H, m,  $\text{CHCH}_2\text{CH}_2$ ), 2.25-2.15 (1H, m,  $\text{CH}_2\text{C}=\text{O}$ ), 2.04-1.94 (2H, m,  $\text{CH}_2\text{C}=\text{O}$ ), 1.88-1.79 (5H, m,  $\text{CH}_3\text{C}=\text{CH}$  and 2 of  $\text{CHCH}_2\text{CH}_2$ ), 1.57-1.47 (1H, m,  $\text{CHCH}_2\text{CH}_2$ ), 1.37-1.26 (1H, m,  $\text{CHCH}_2\text{CH}_2$ ),  $\text{NH}$  not observed;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.6 (C), 152.2 (C), 142.9 (C), 142.5 (C), 137.5 (C), 137.4 (C), 128.5 ( $2 \times \text{CH}$ ), 127.1 (CH), 126.3 ( $2 \times \text{CH}$ ), 125.3 (CH), 123.2 (CH), 114.9 ( $2 \times \text{CH}$ ), 114.3 ( $2 \times \text{CH}$ ), 55.8 ( $\text{CH}_3$ ), 47.9 ( $\text{CH}_2$ ), 42.5 ( $\text{CH}_2$ ), 41.3 ( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 38.2 (CH), 36.3 ( $\text{CH}_2$ ), 31.3 ( $\text{CH}_2$ ), 25.1 ( $\text{CH}_2$ ), 16.6 ( $\text{CH}_3$ ).

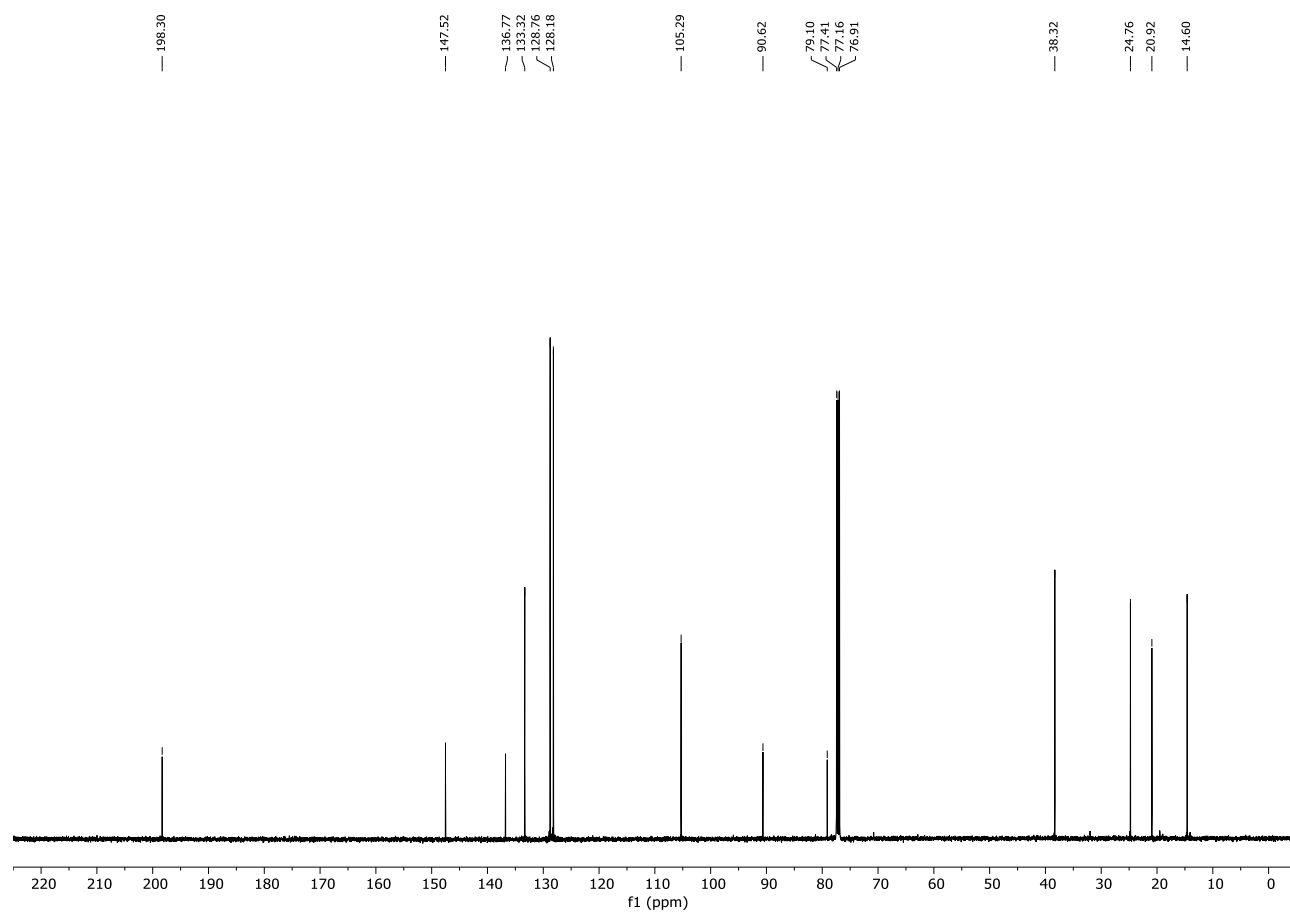
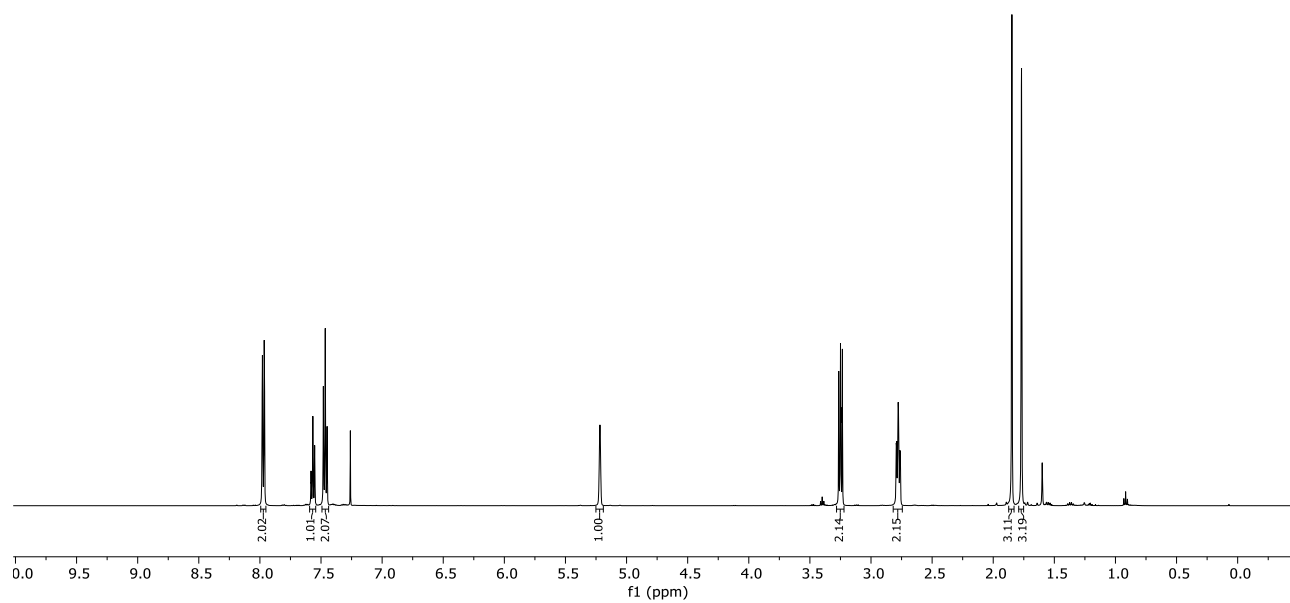
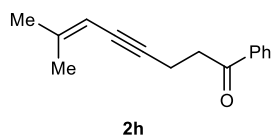
*Characteristic NMR data of minor Z-isomer:*  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.30 (1H, dd,  $J = 11.4, 1.5$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ ), 2.55 (2H, t,  $J = 6.9$  Hz,  $\text{CH}_2$ ), 1.92 (3H, d,  $J = 1.5$  Hz,  $\text{CH}_3\text{C}=\text{CH}$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  124.1 (CH), 32.2 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_3$ ).

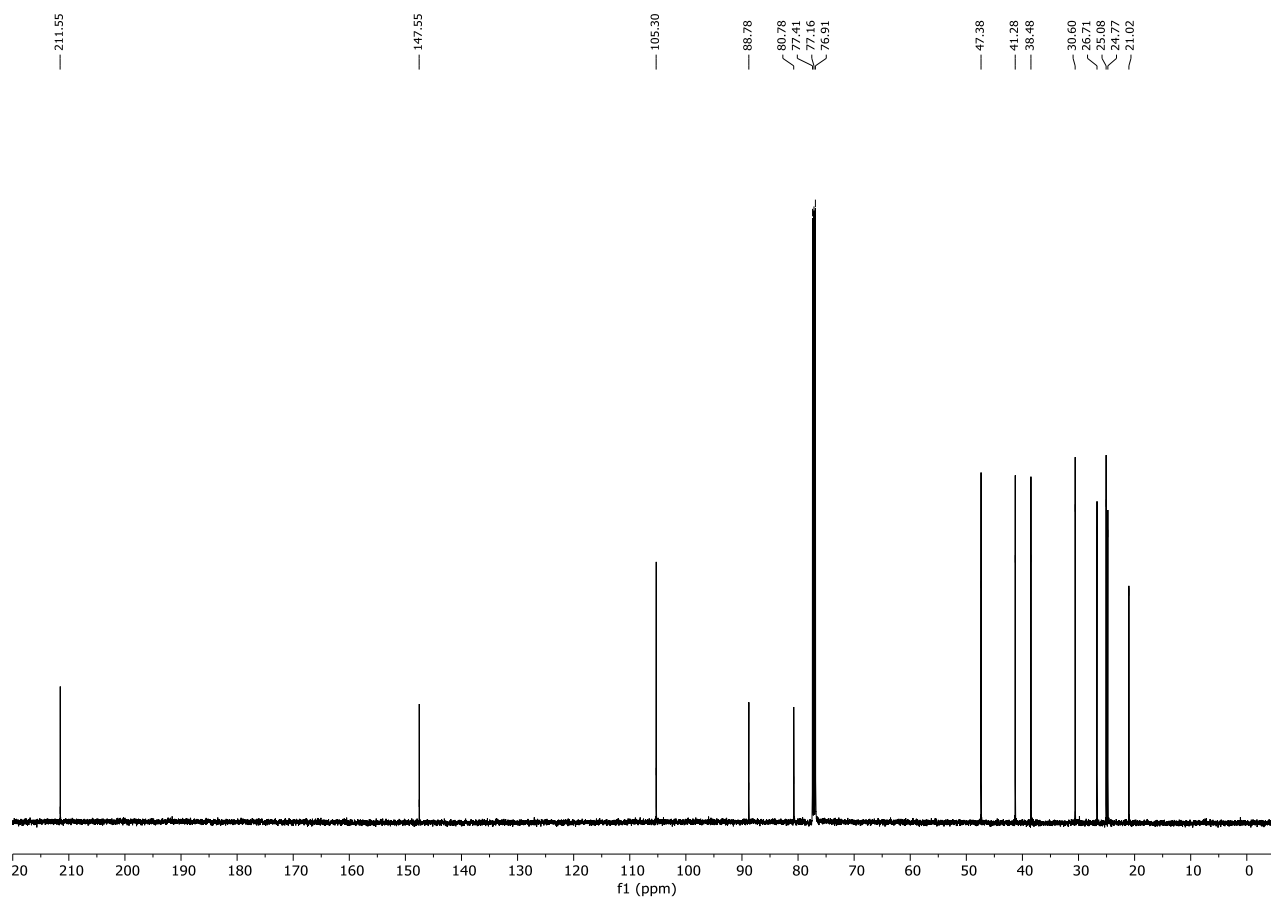
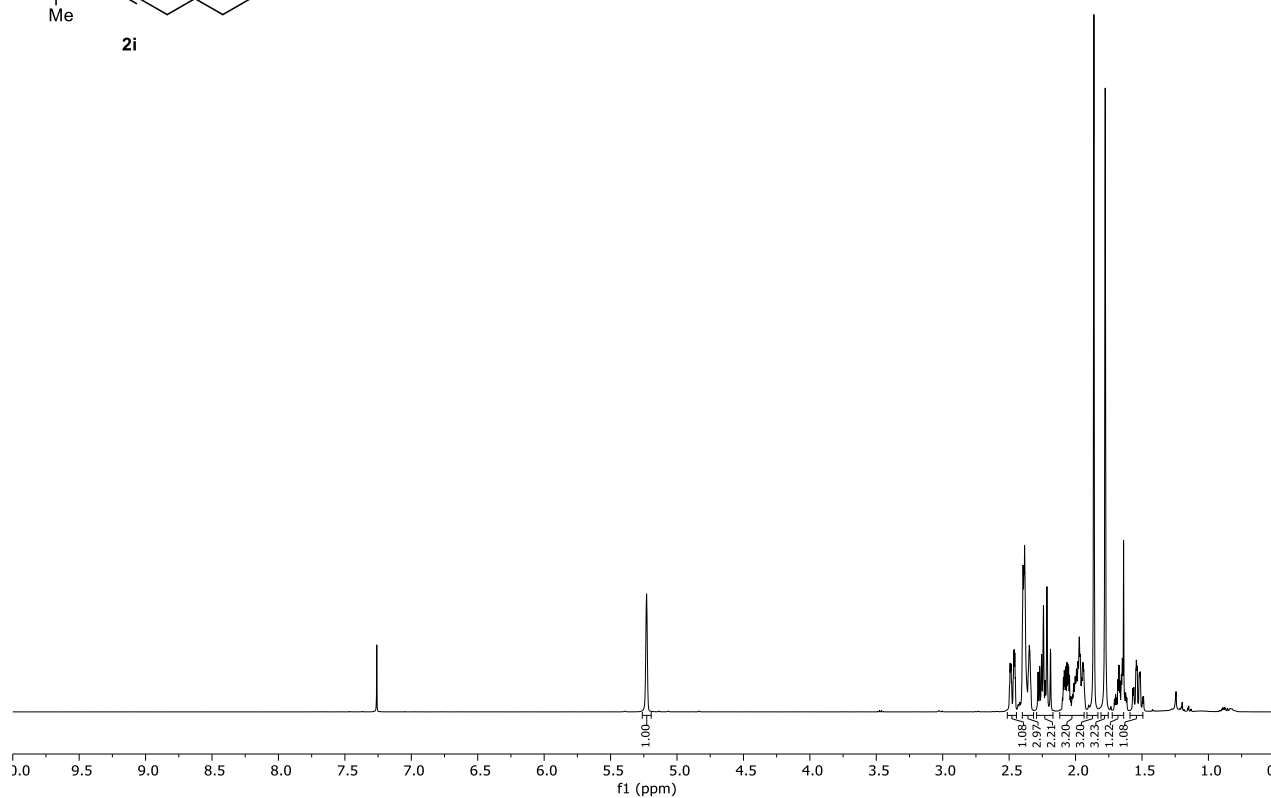
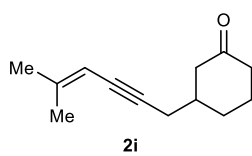
## NMR Spectra

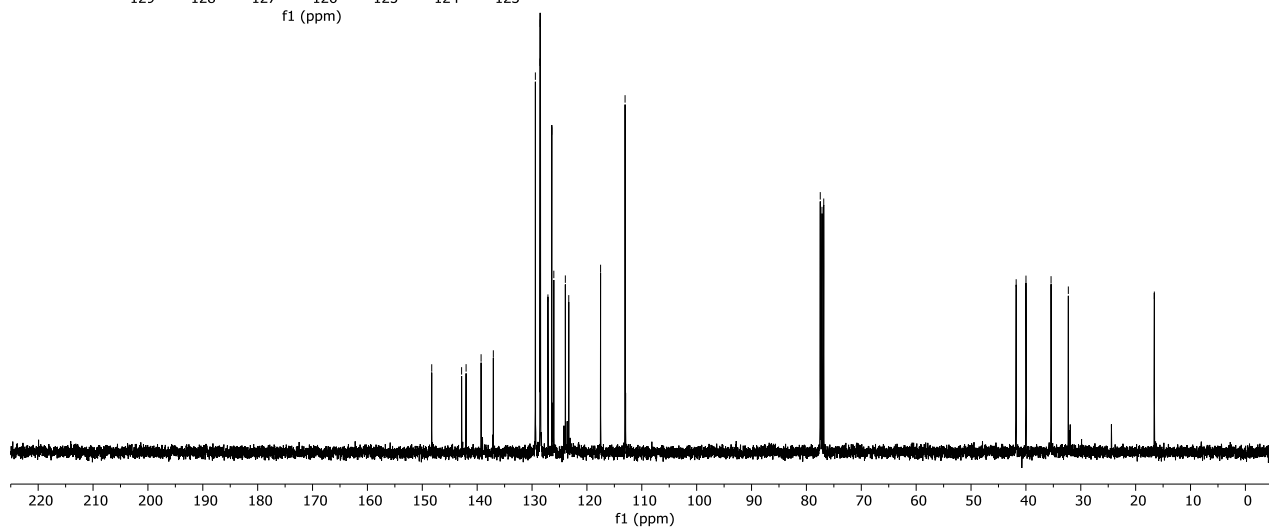
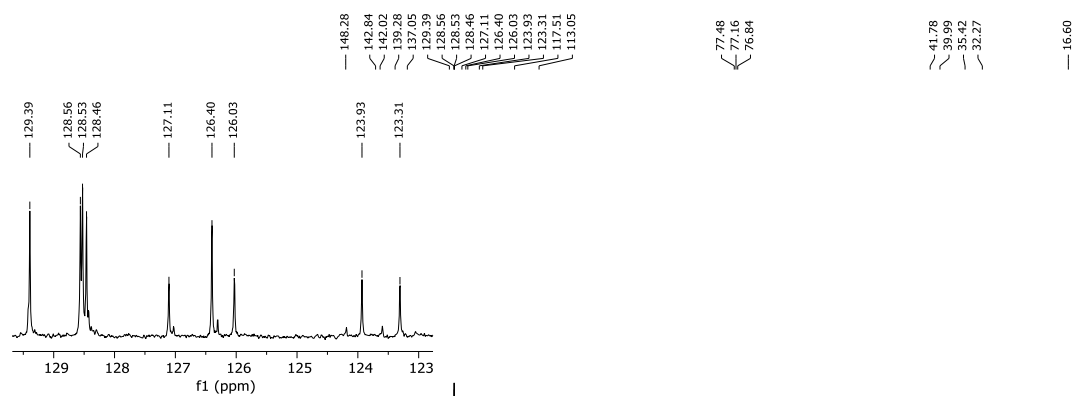
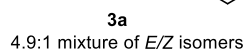


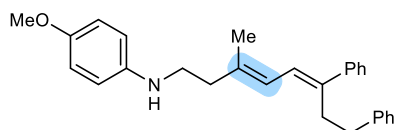
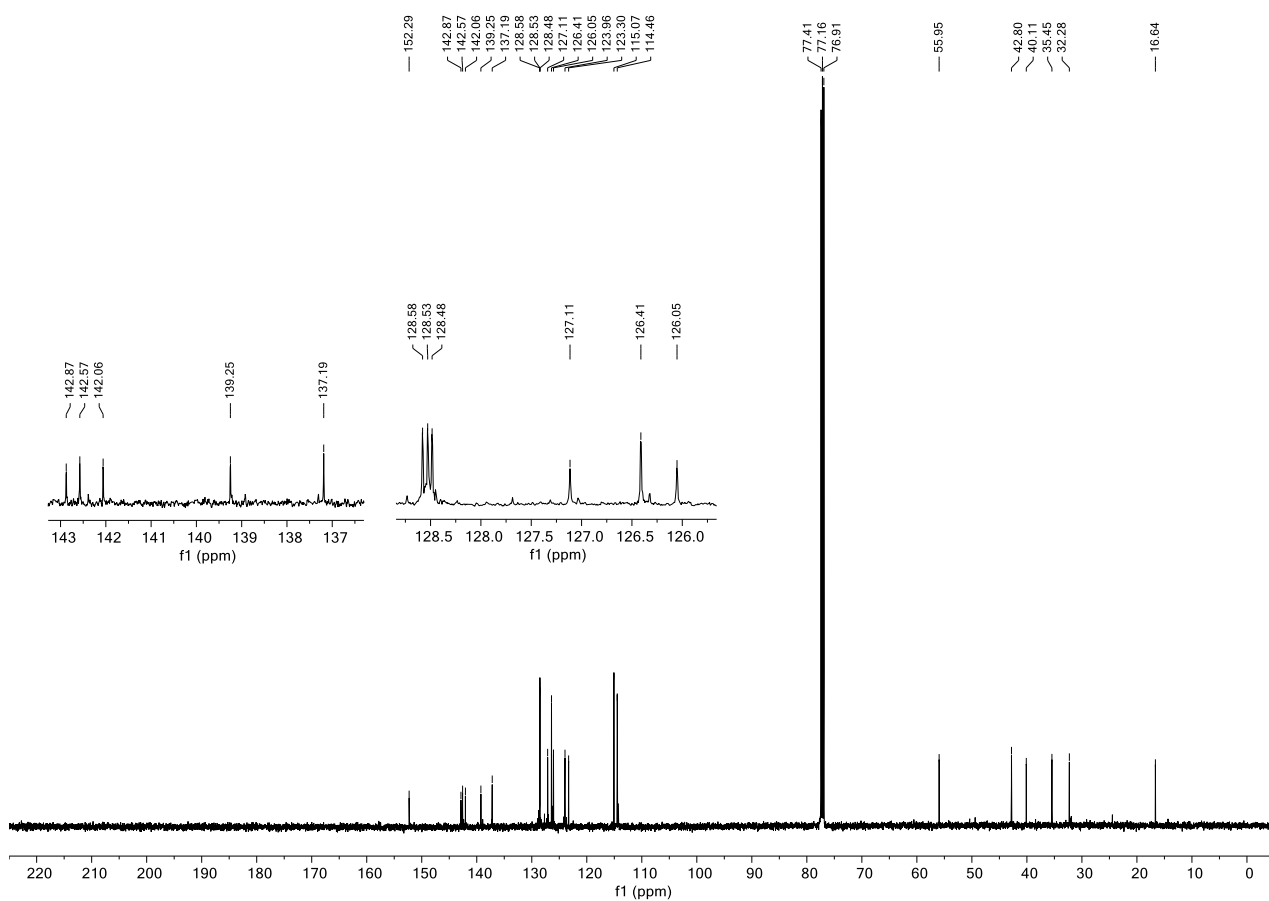
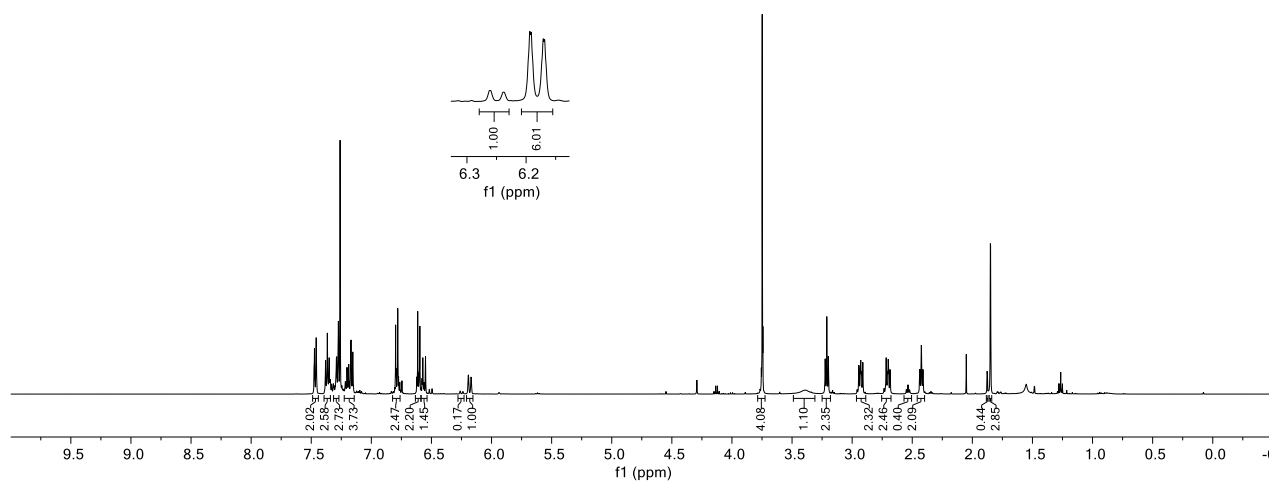


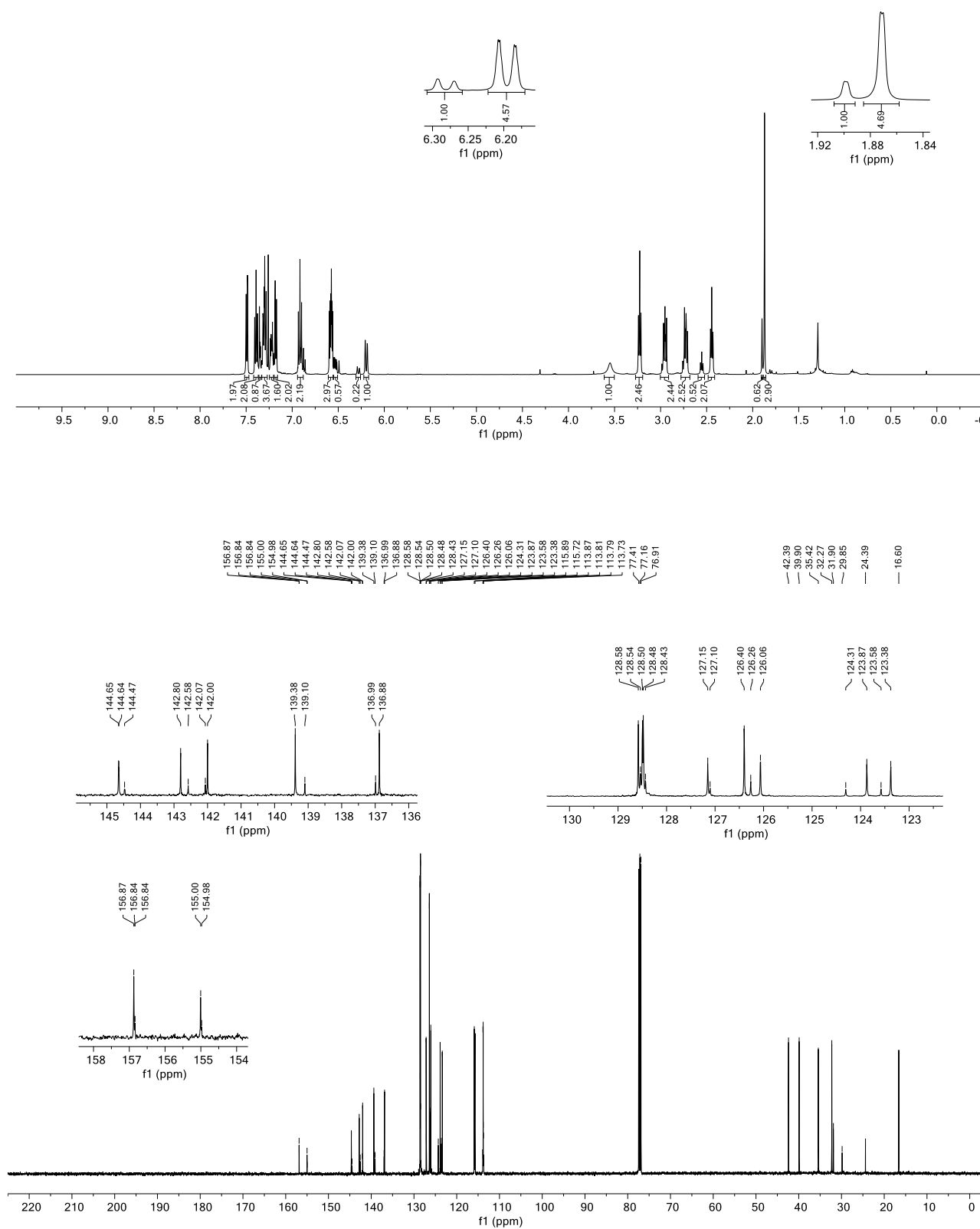
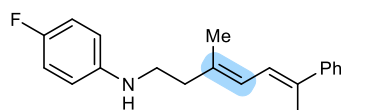


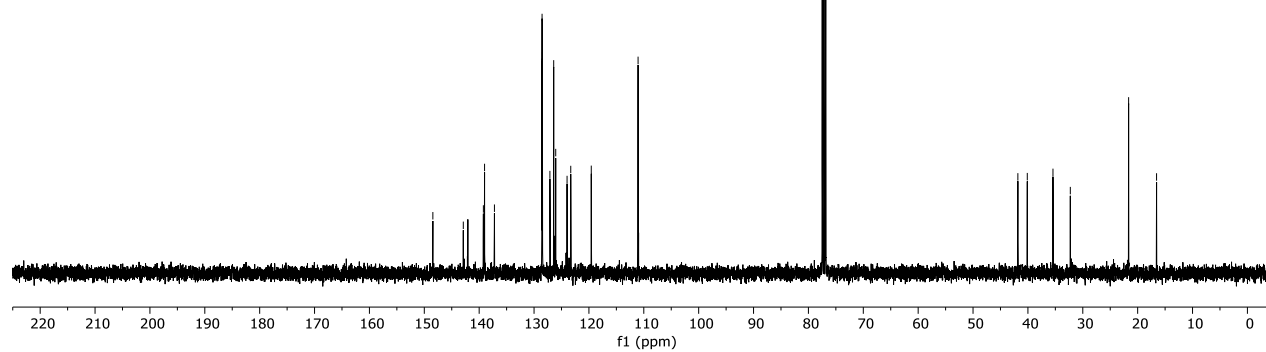
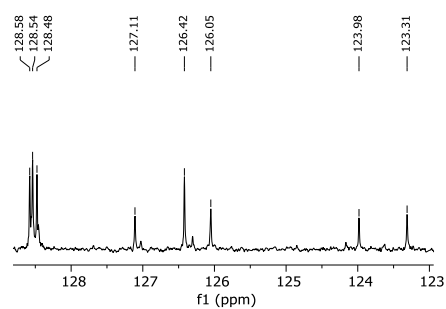
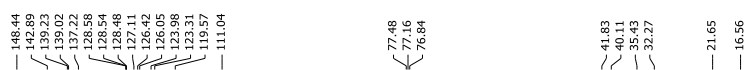
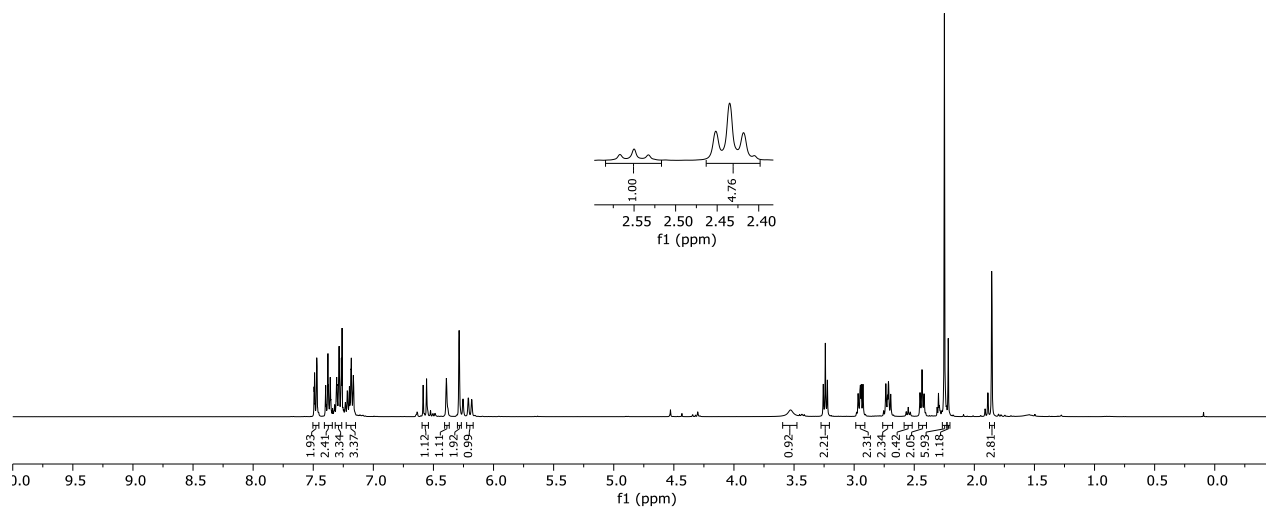
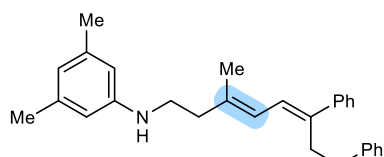


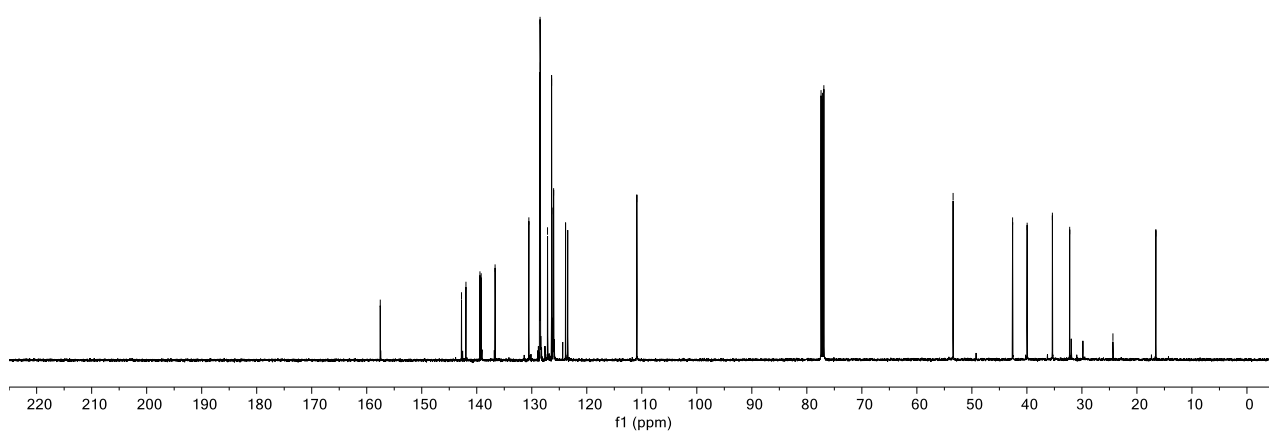
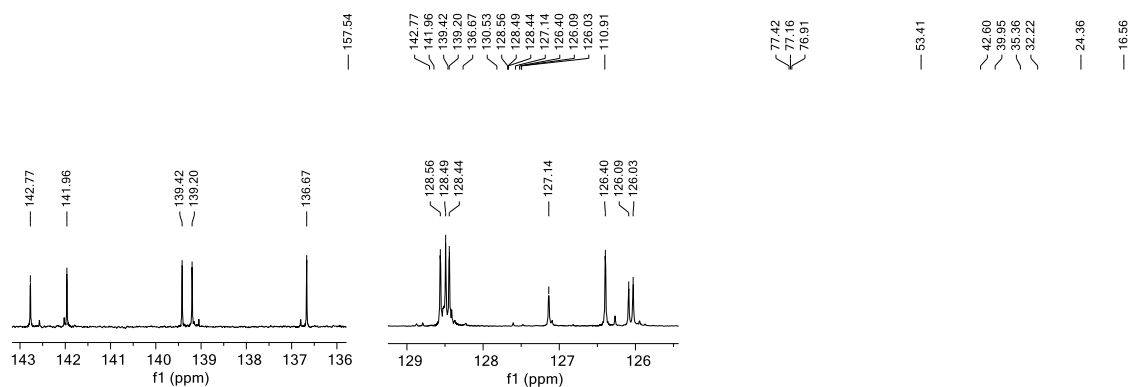
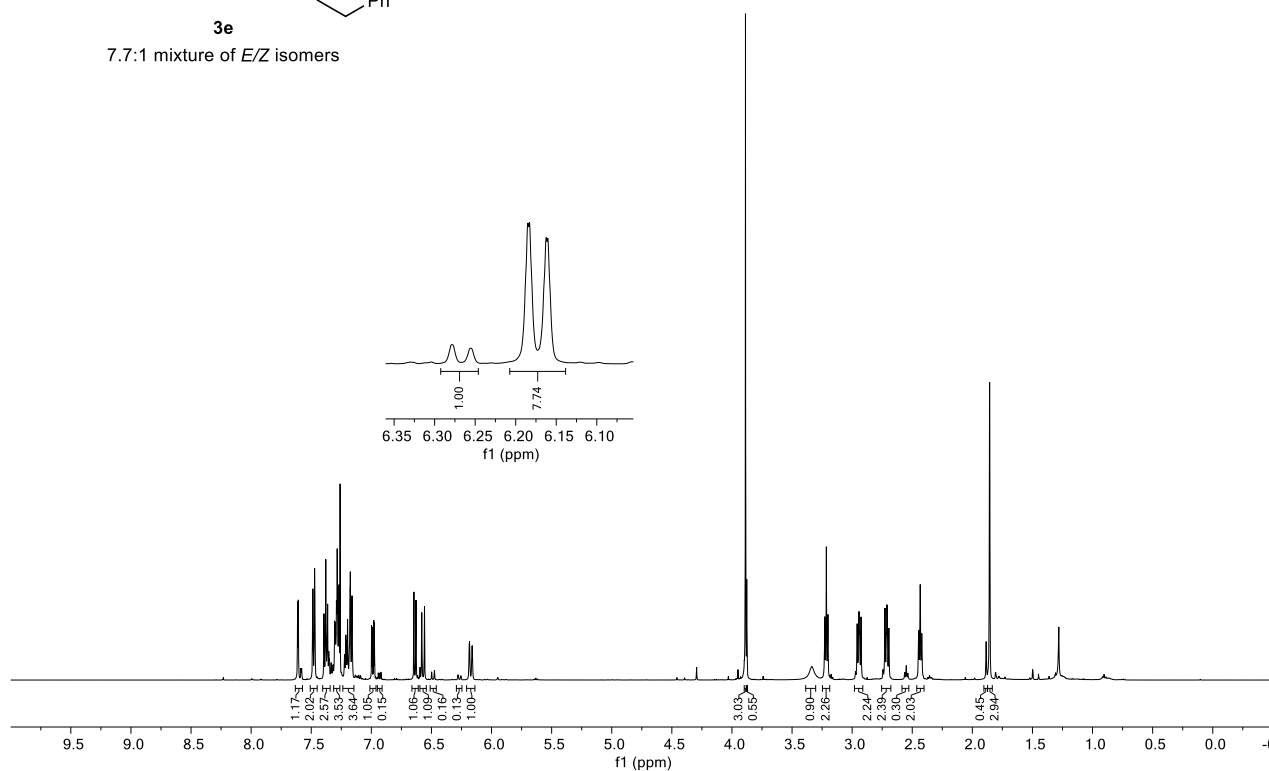
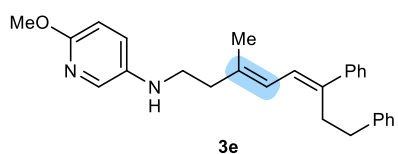




**3b**6.0:1 mixture of *E/Z* isomers

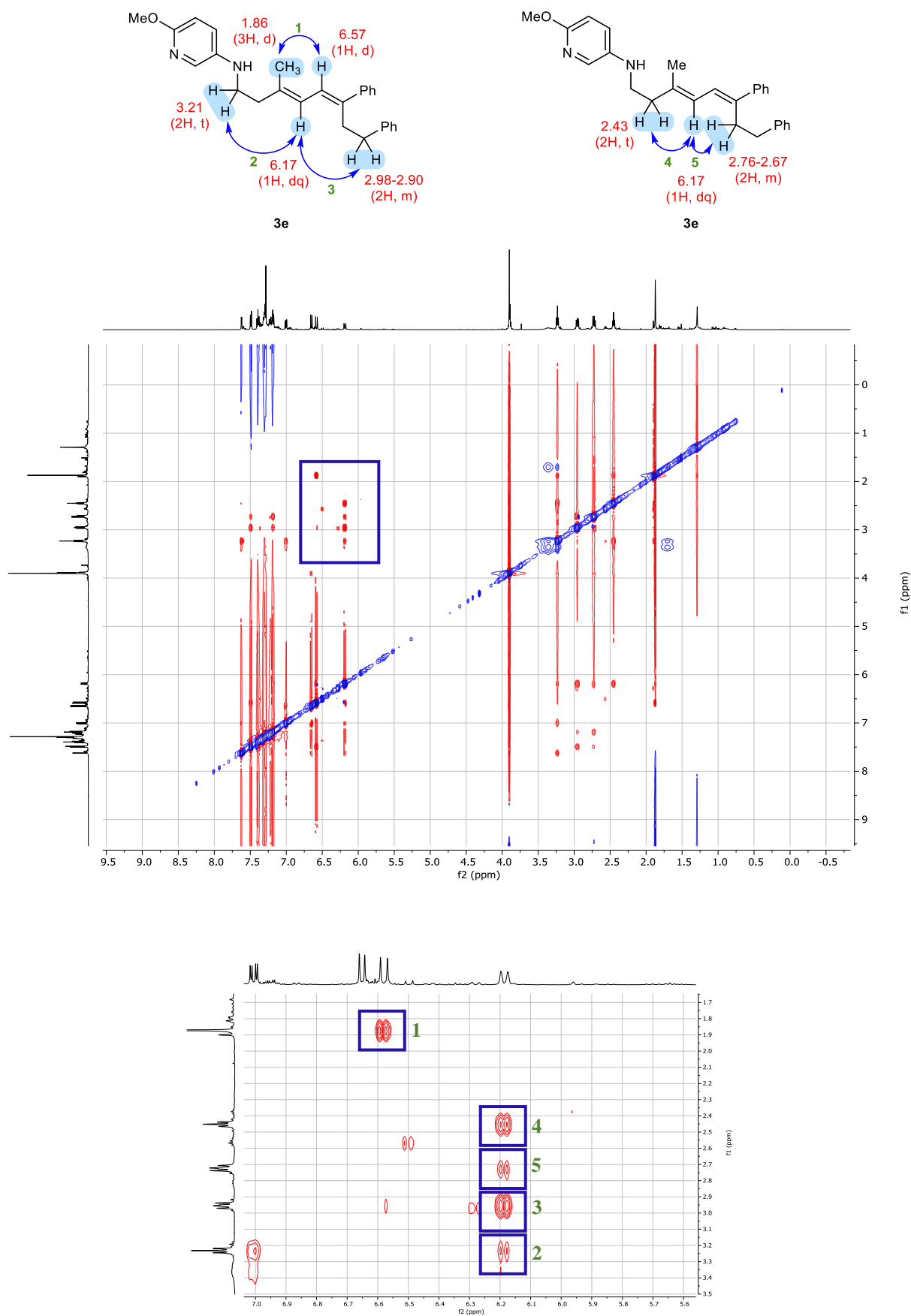


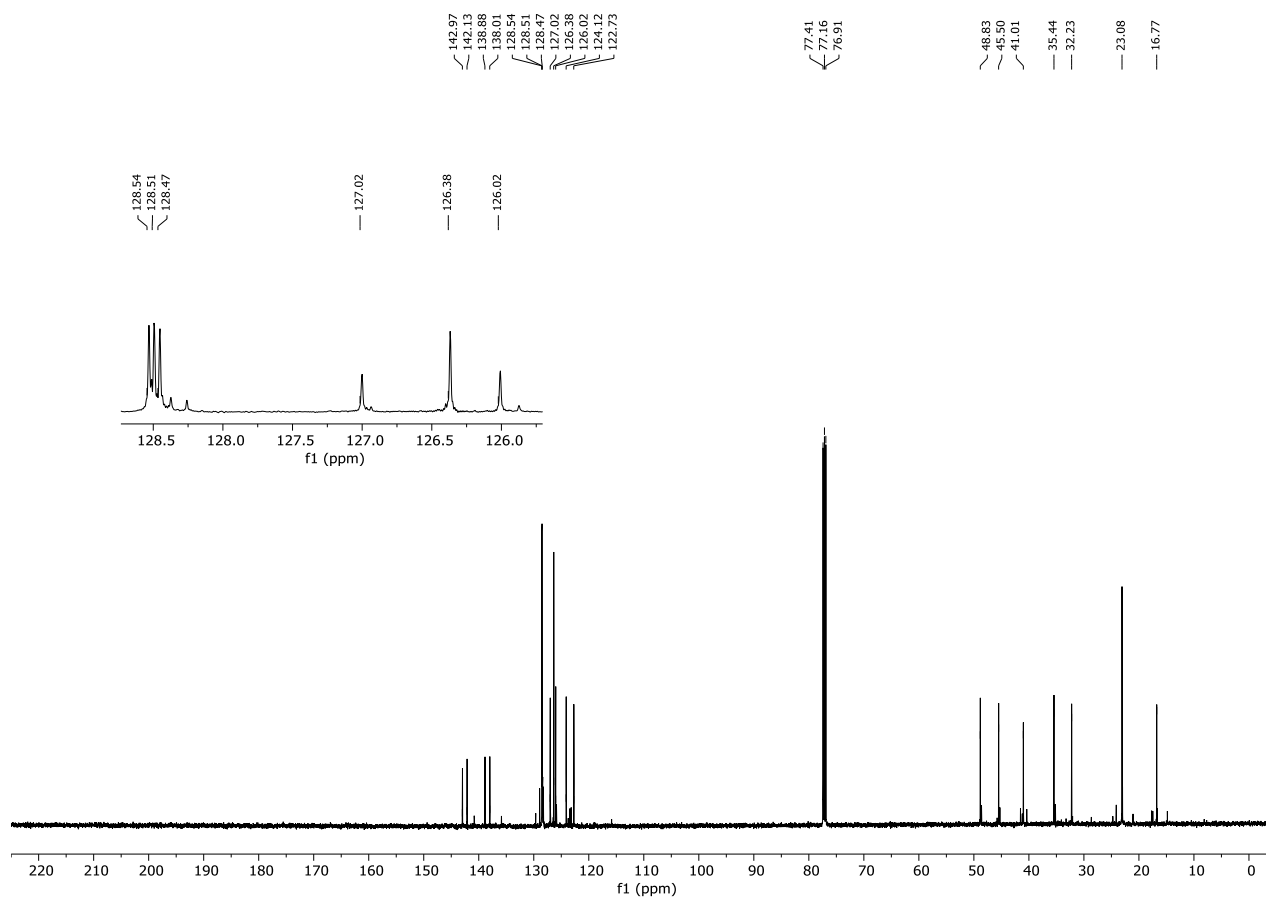
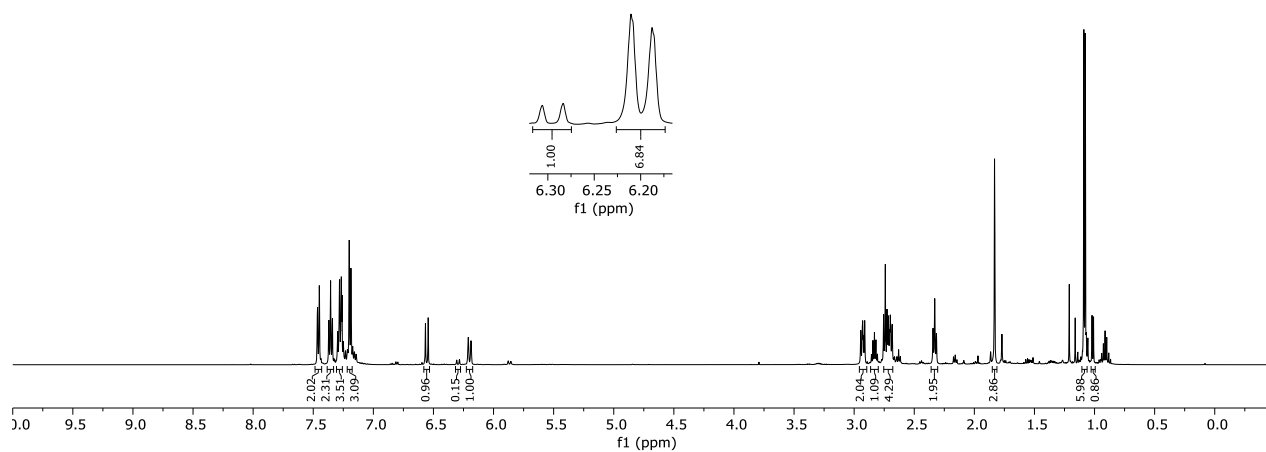
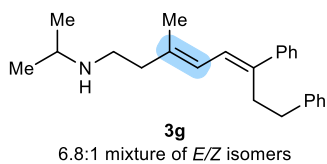


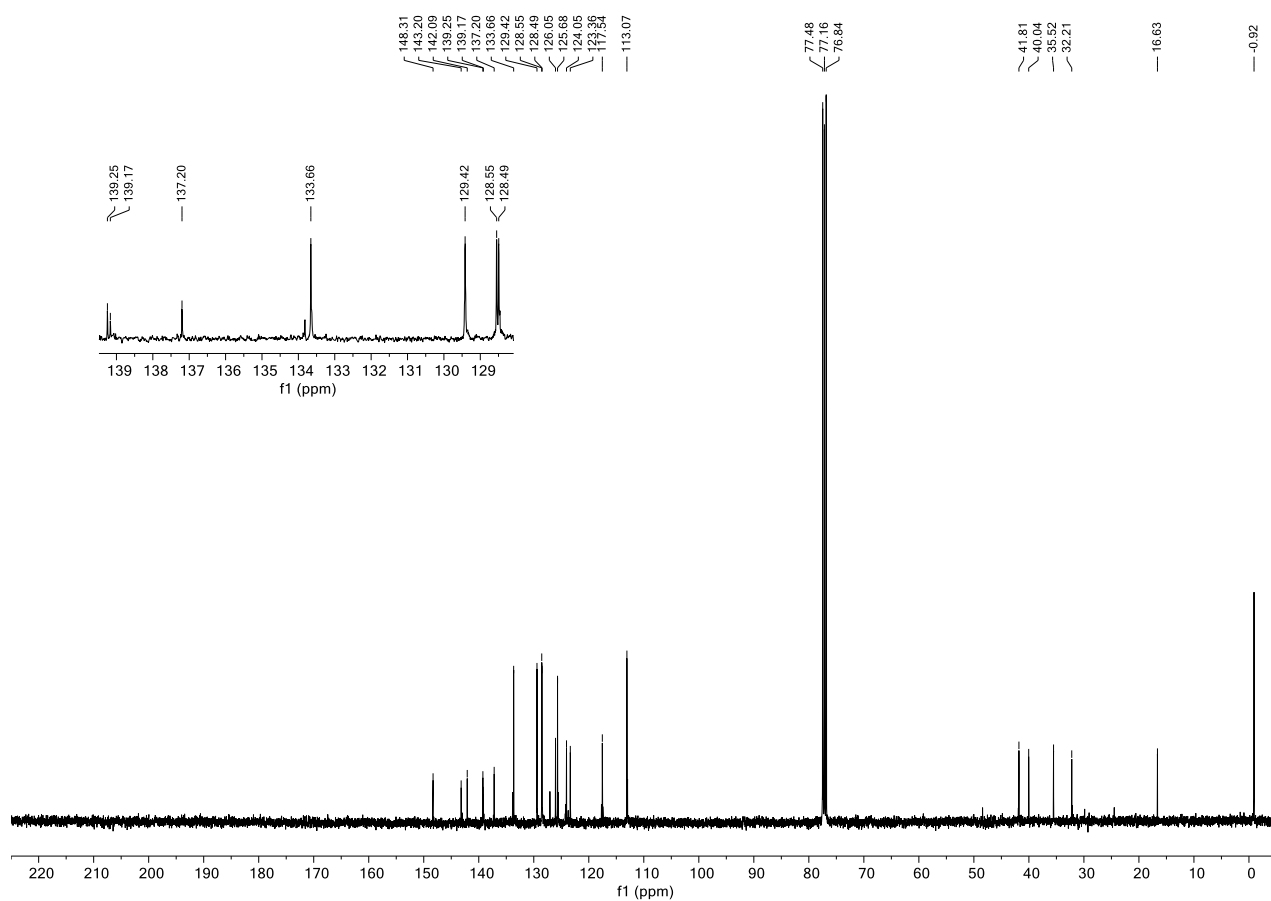
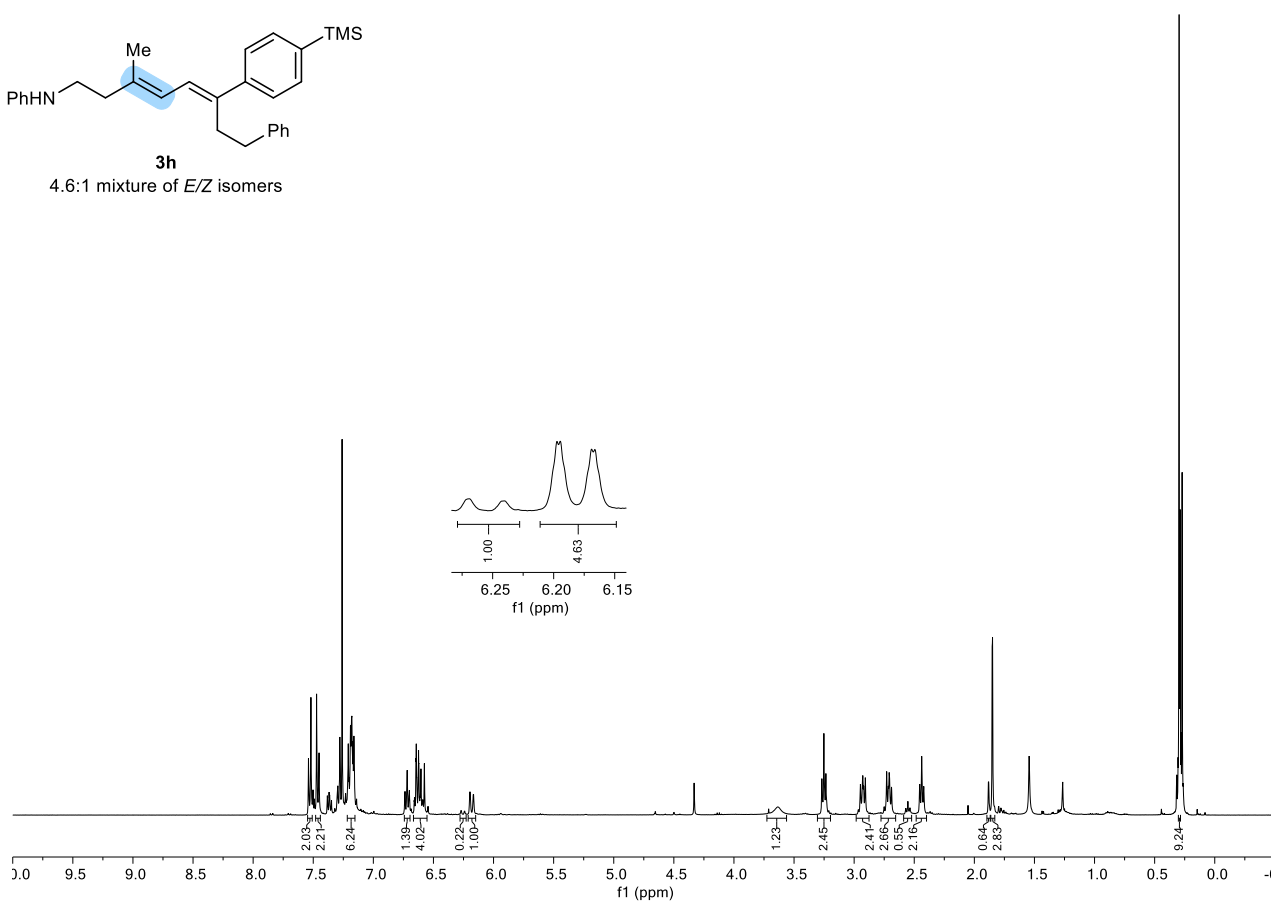
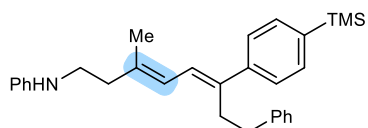




## NOESY Spectrum

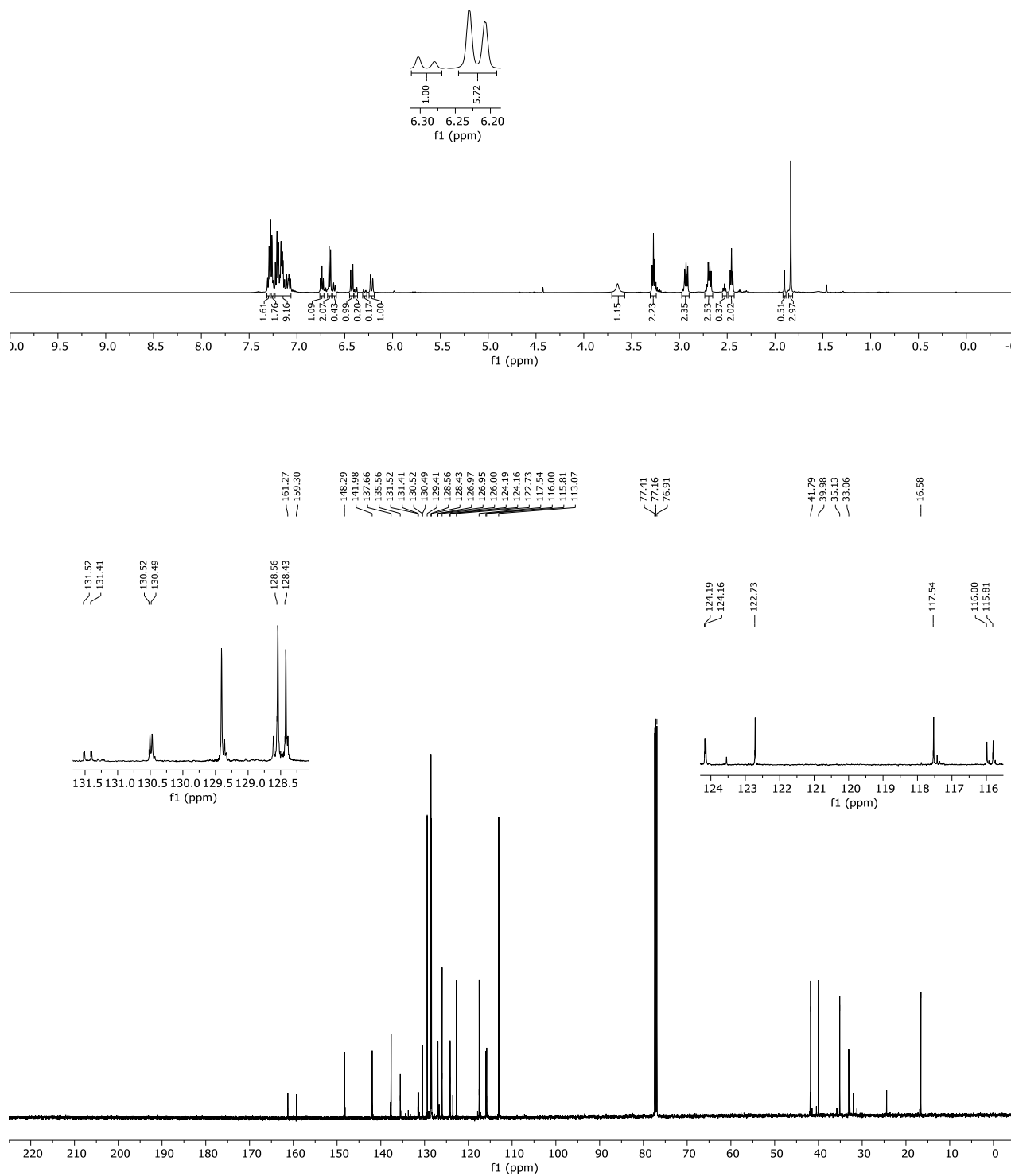


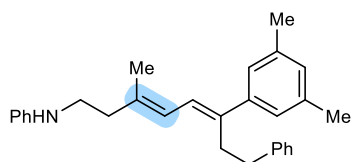




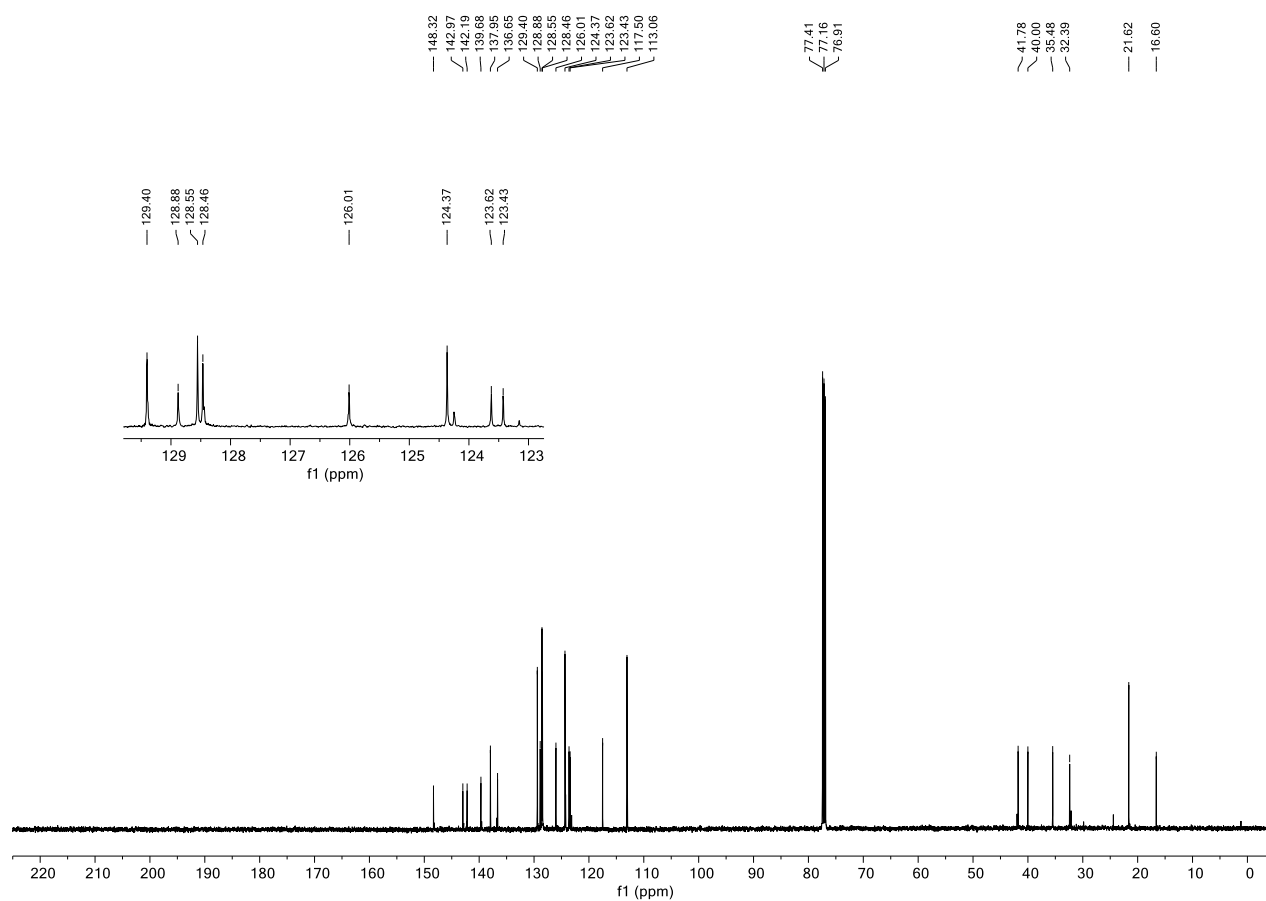
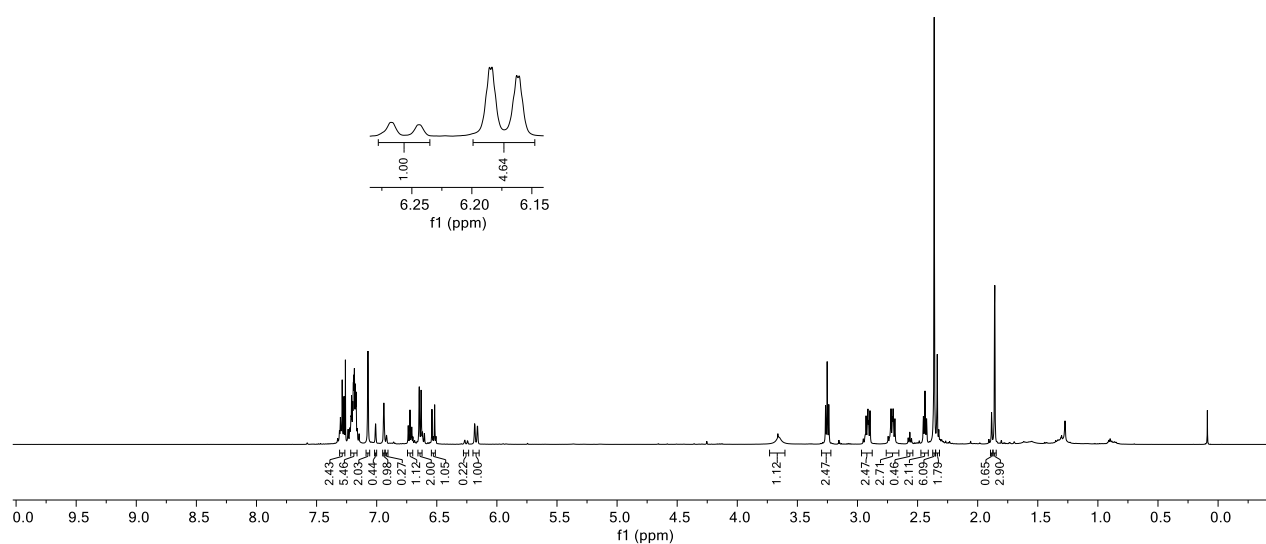


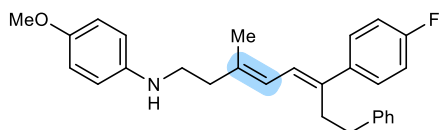
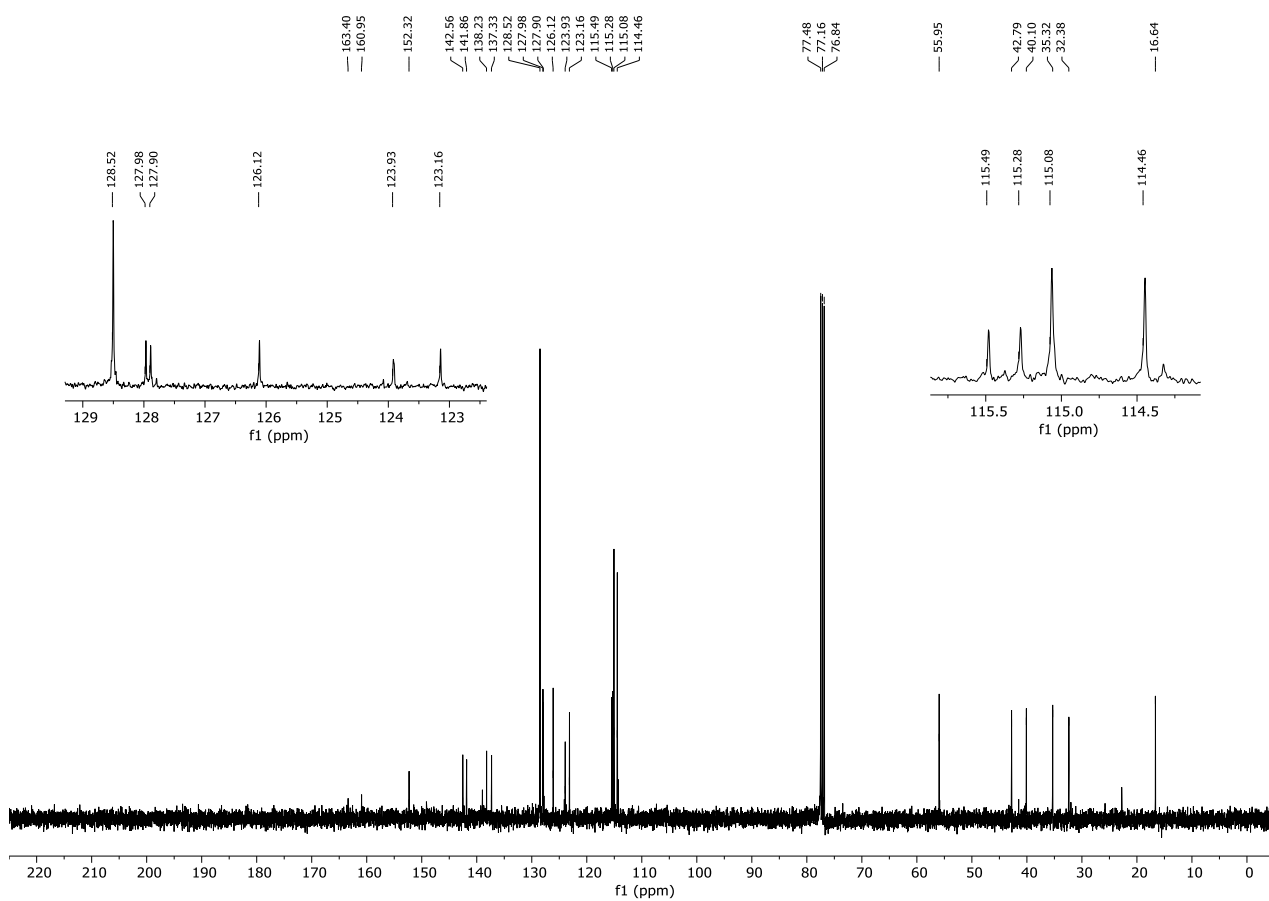
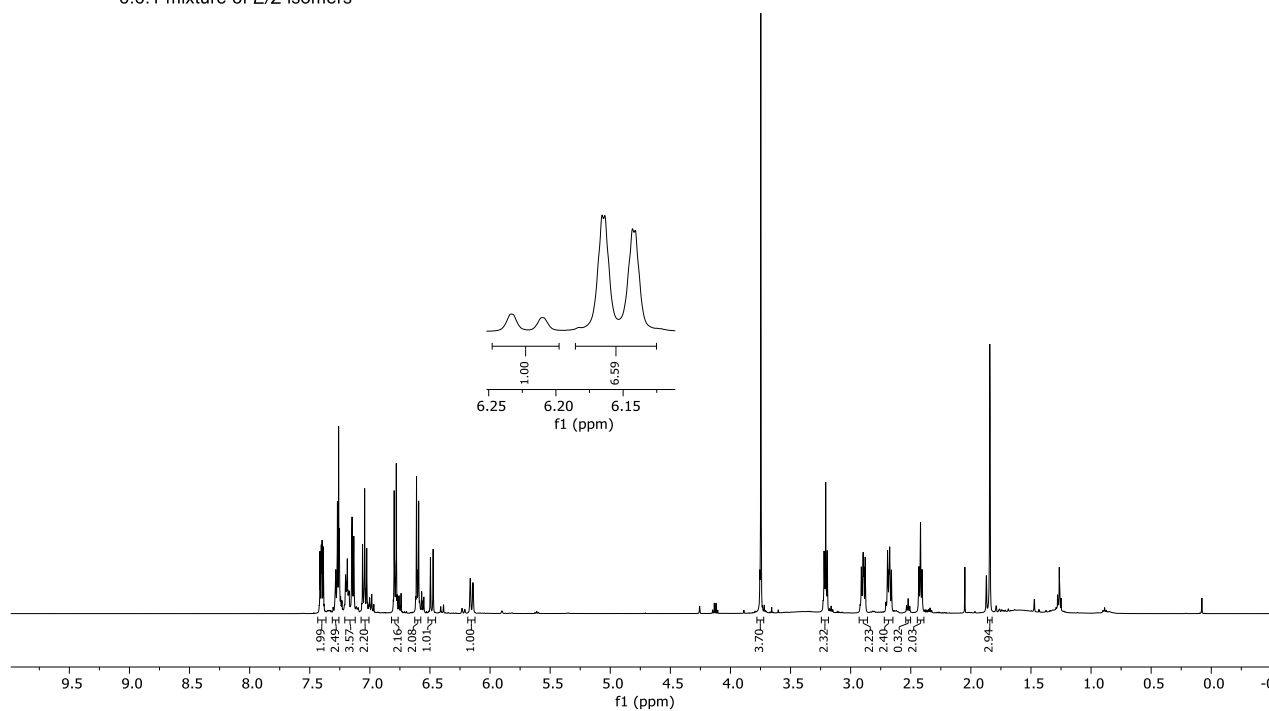
5.7:1 mixture of *E/Z* isomers

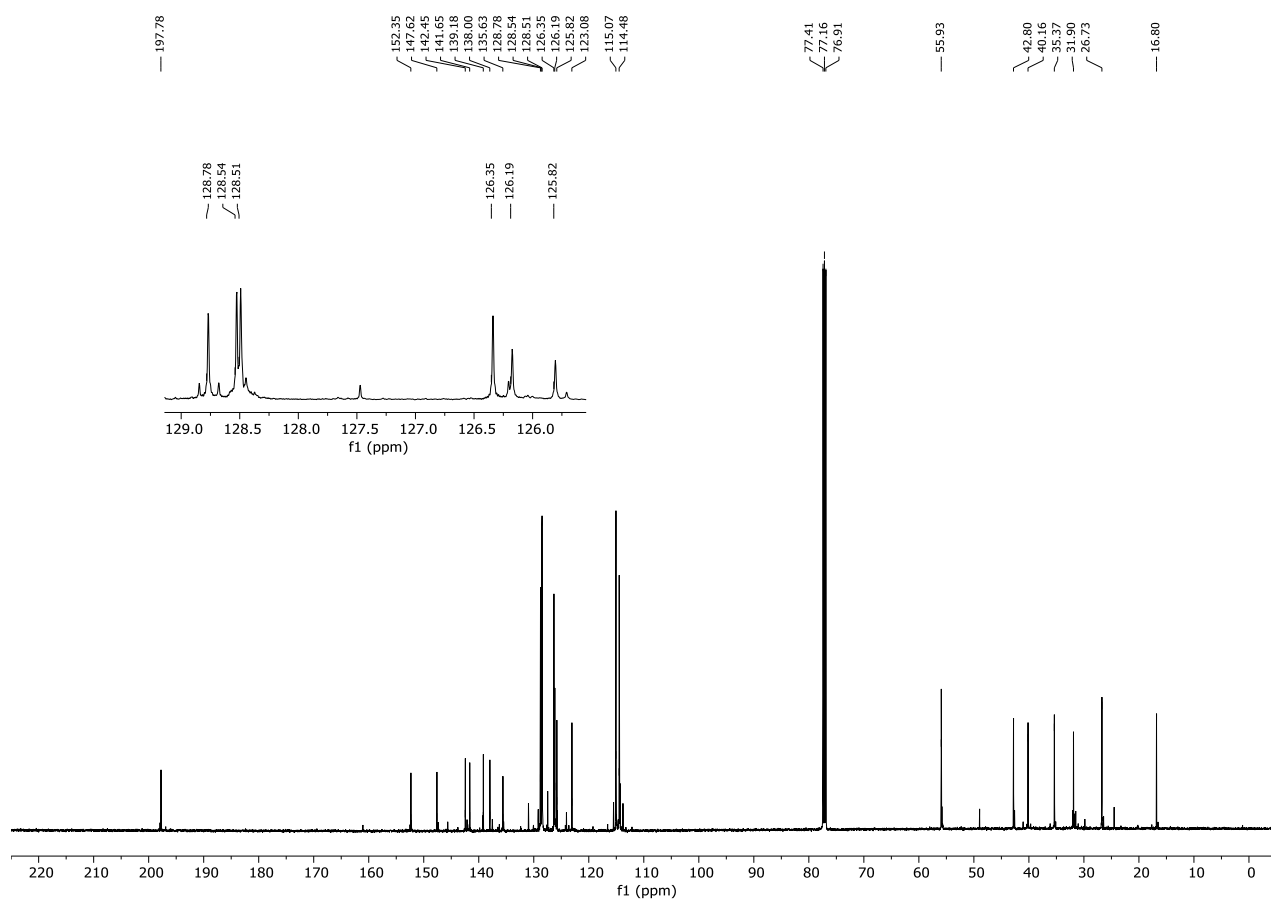
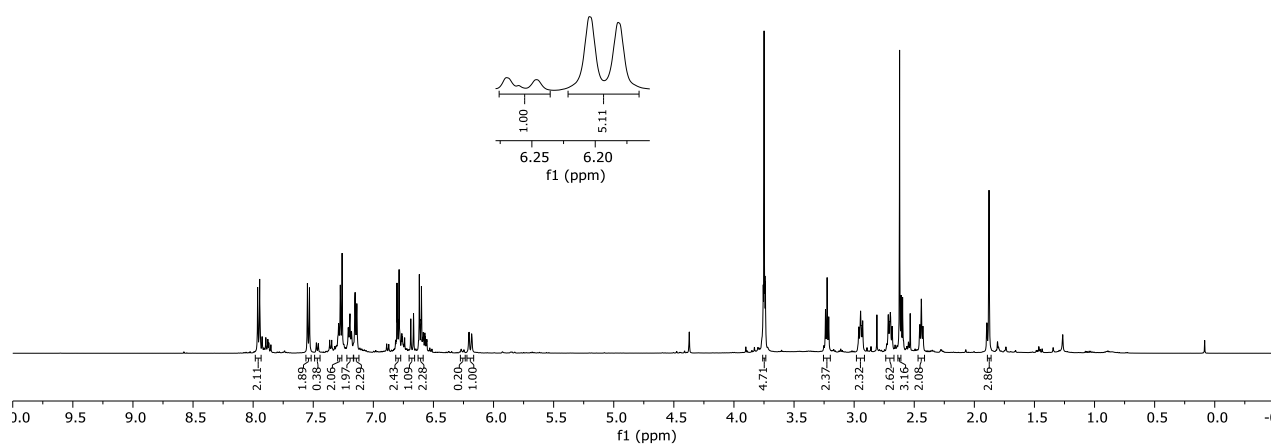
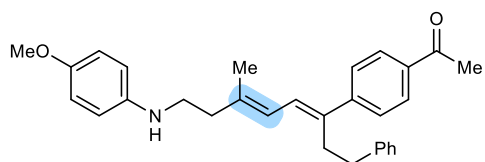


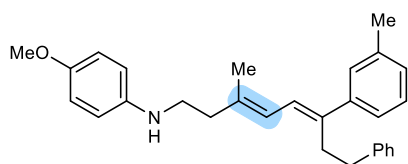


4.6:1 mixture of *E/Z* isomers

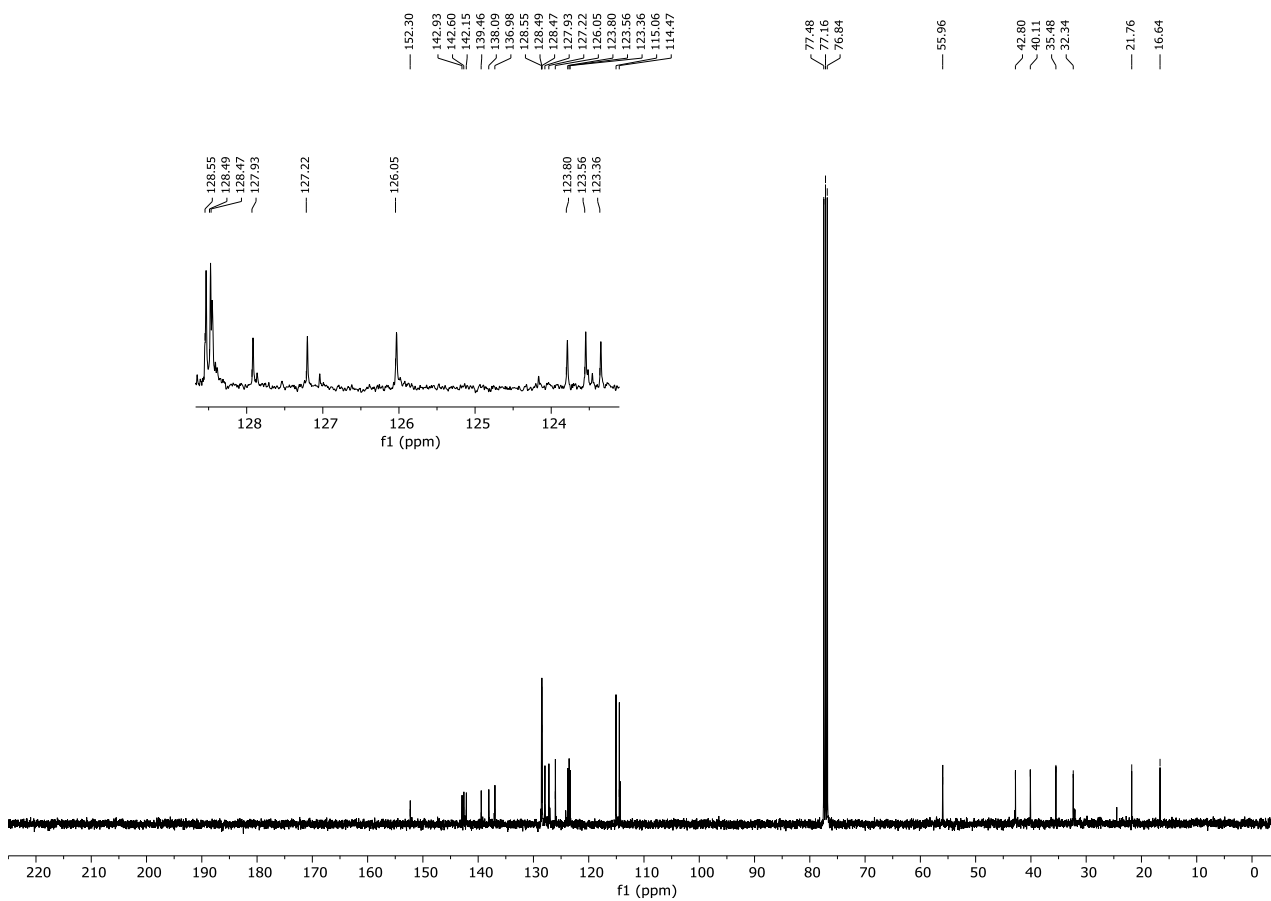
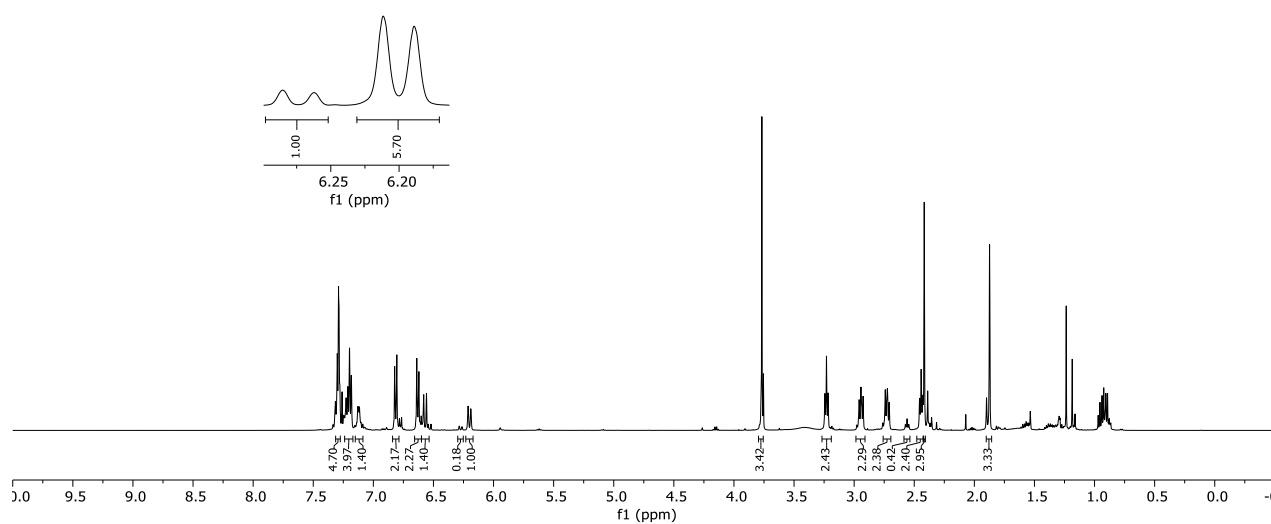


6.6:1 mixture of *E/Z* isomers

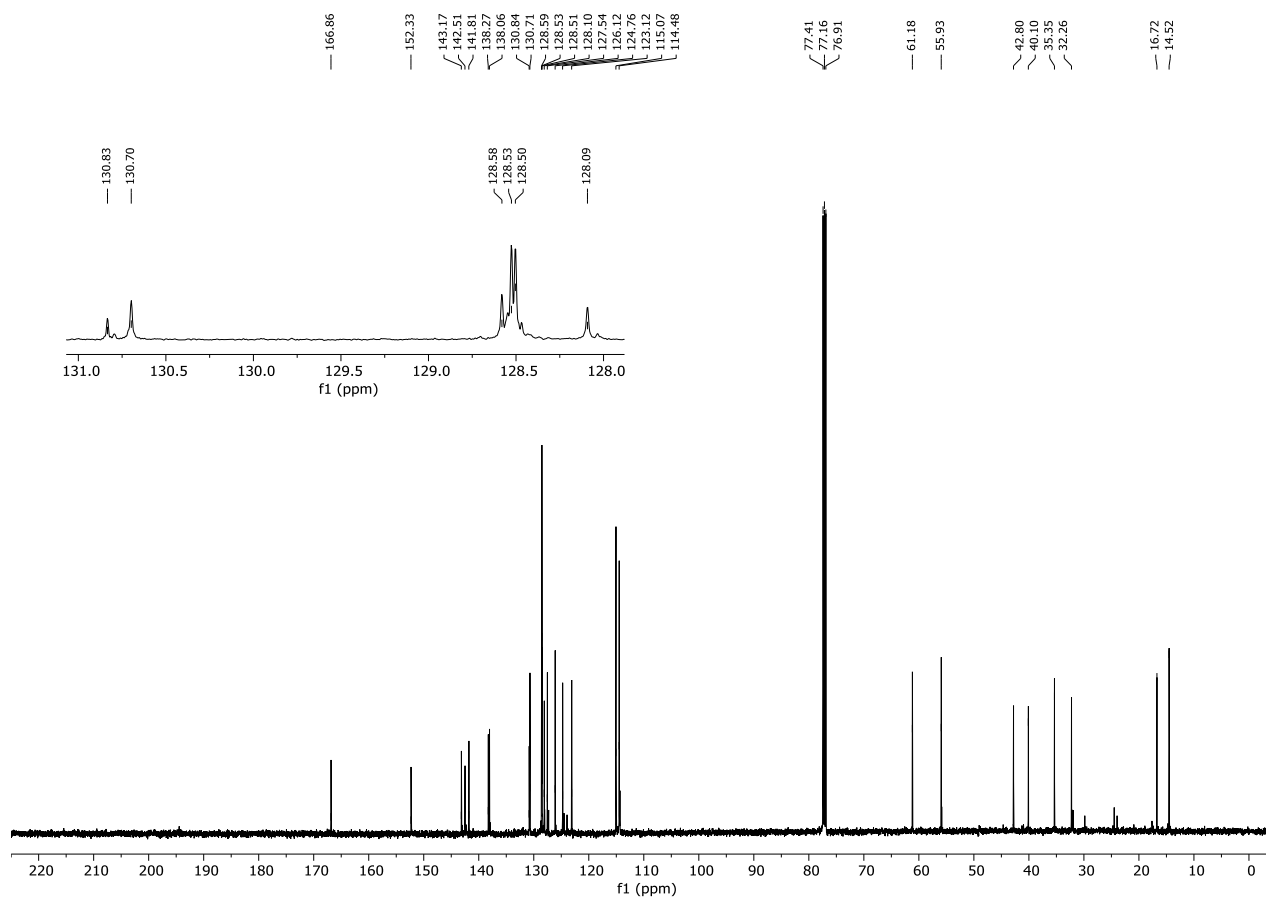
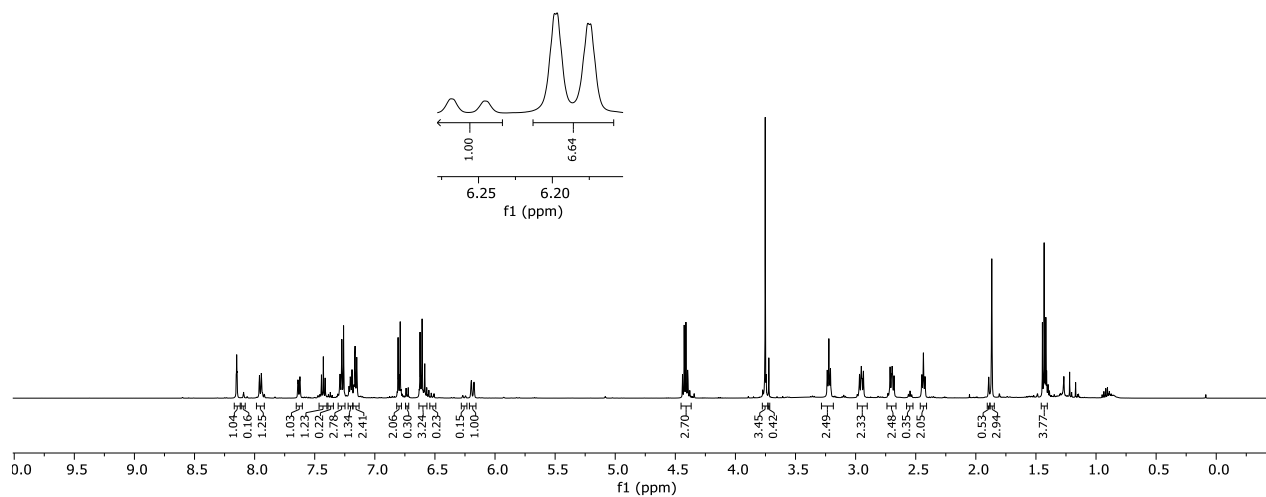
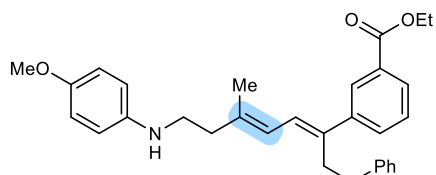


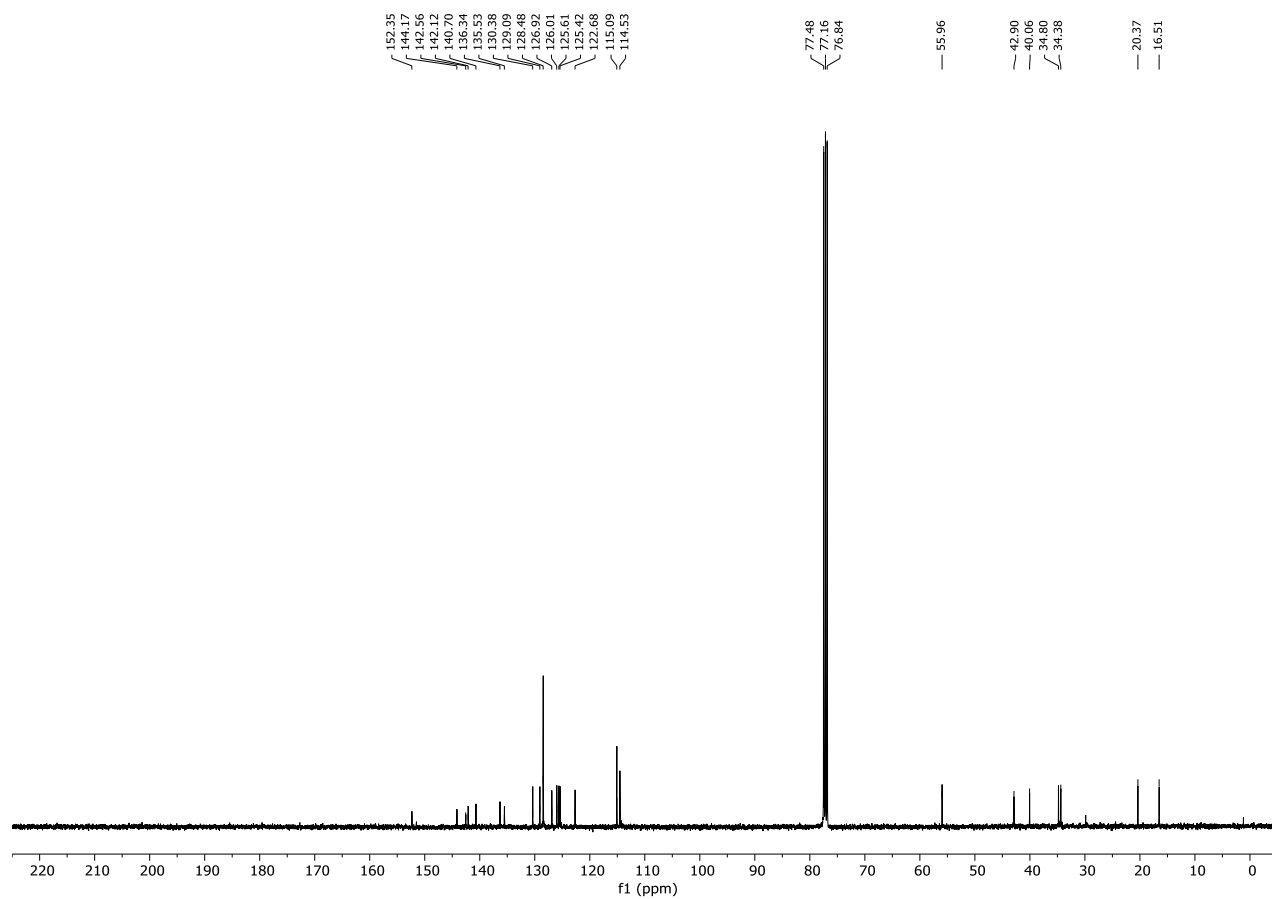
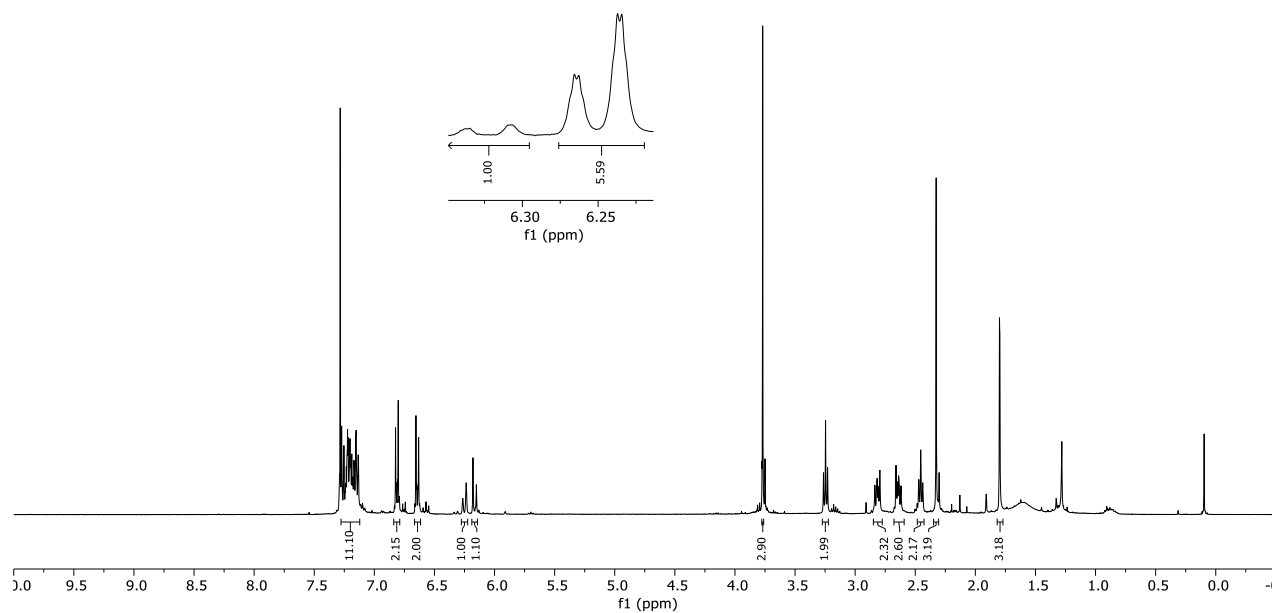
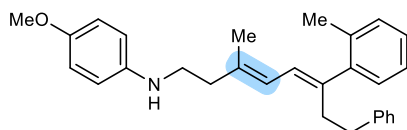


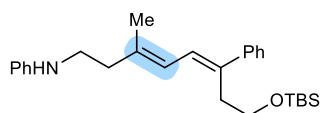
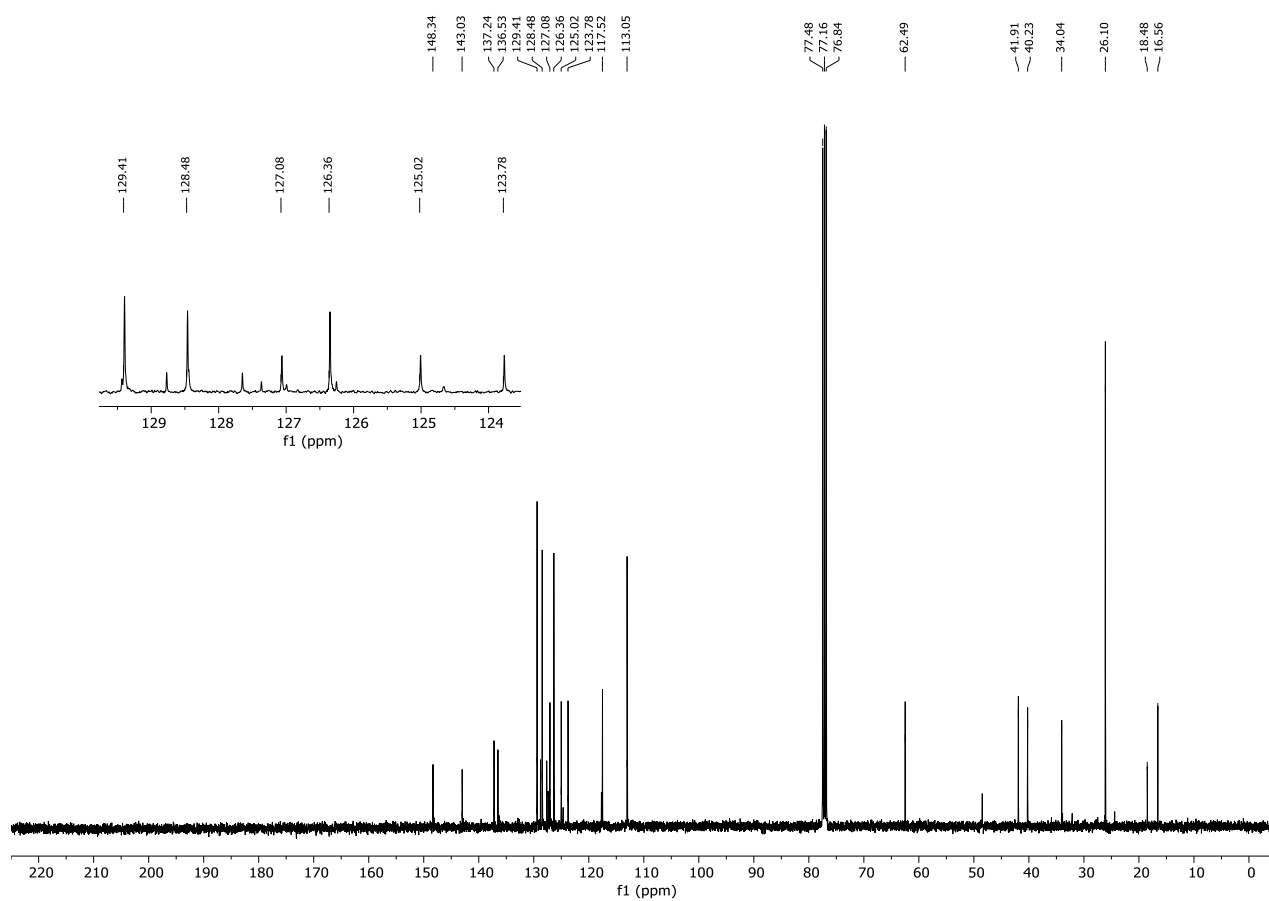
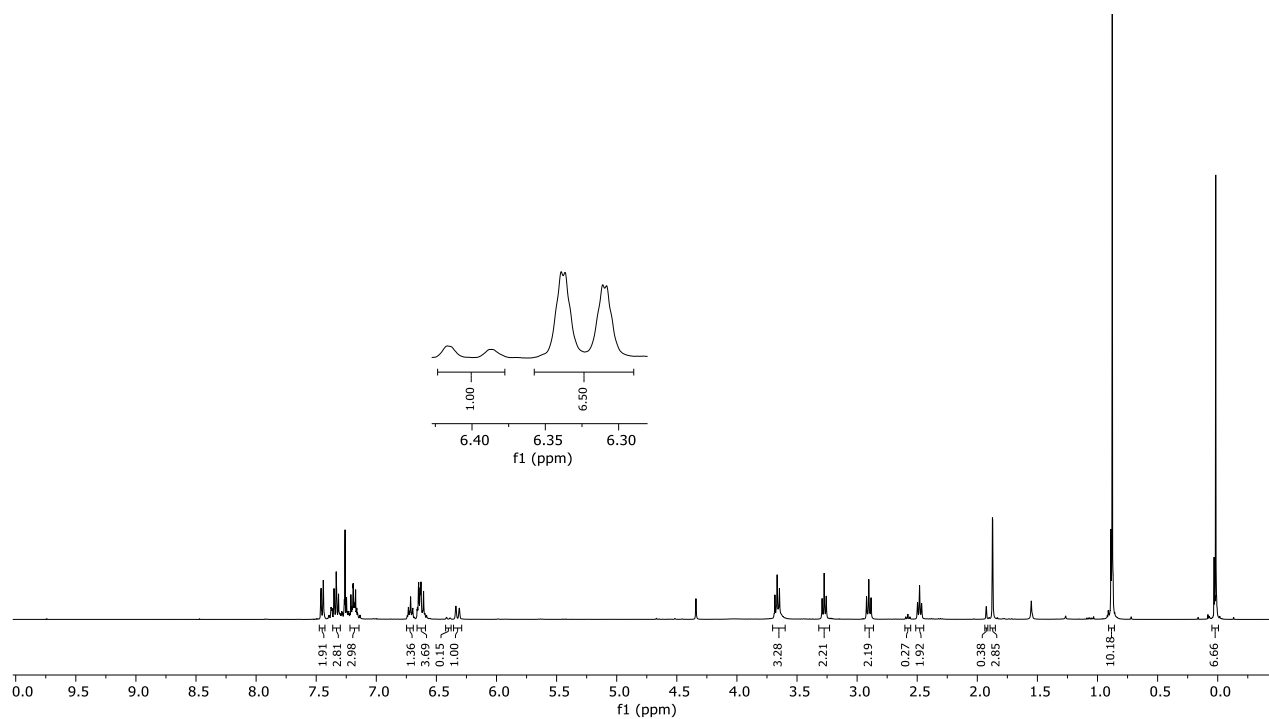
**3m**  
5.7:1 mixture of *E/Z* isomers

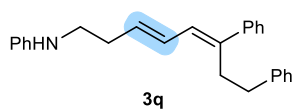




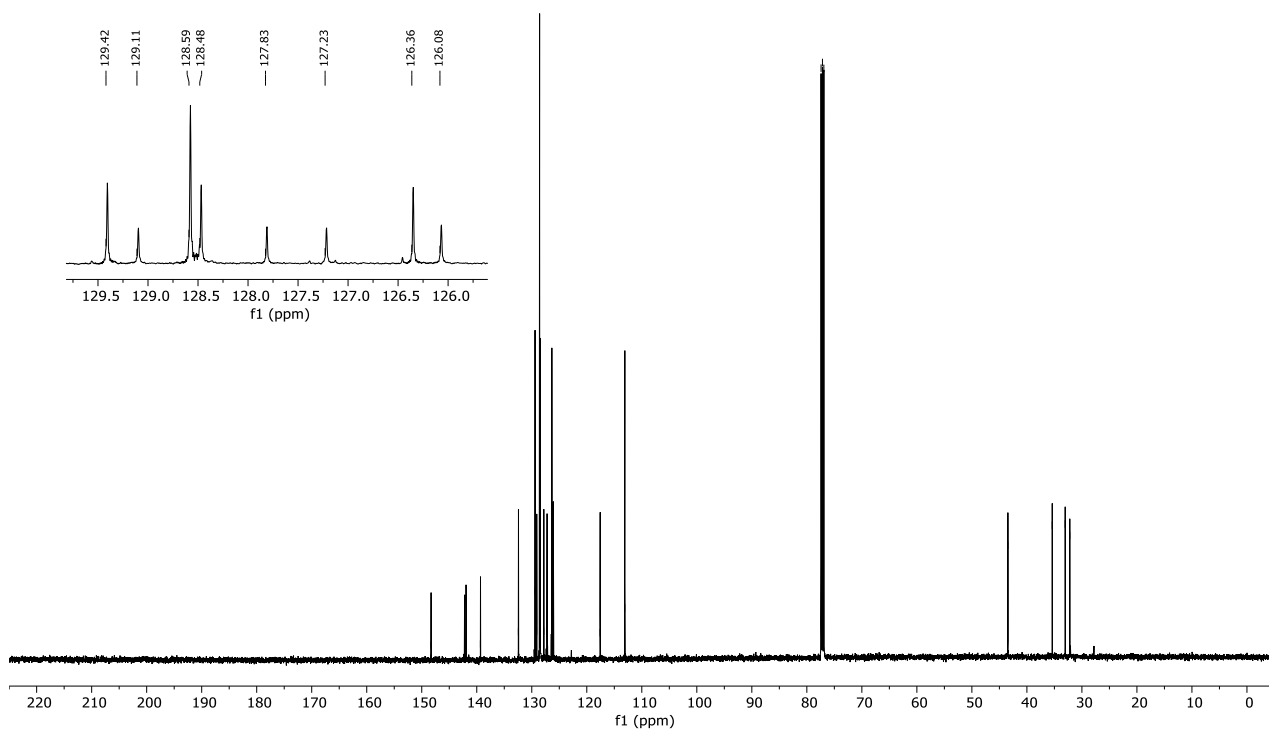
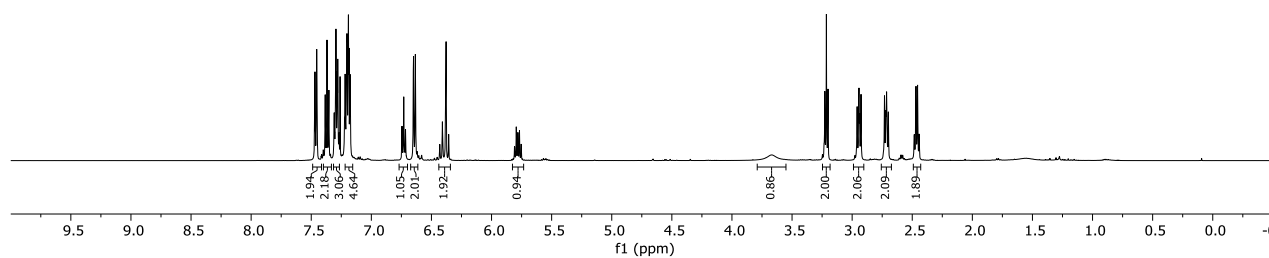
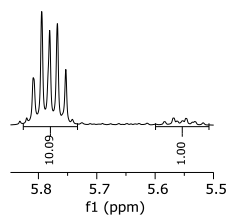




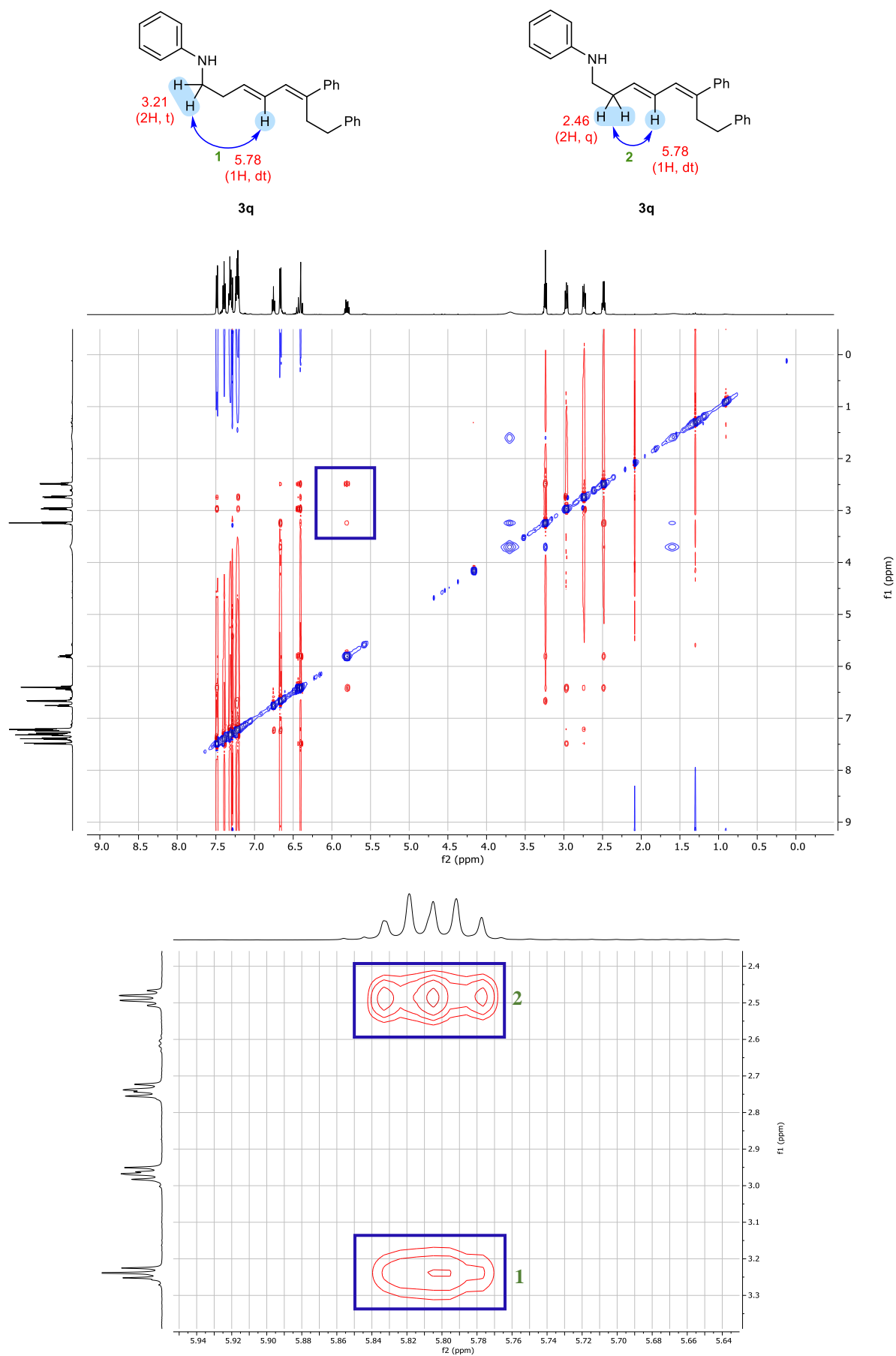
6.5:1 mixture of *E/Z* isomers

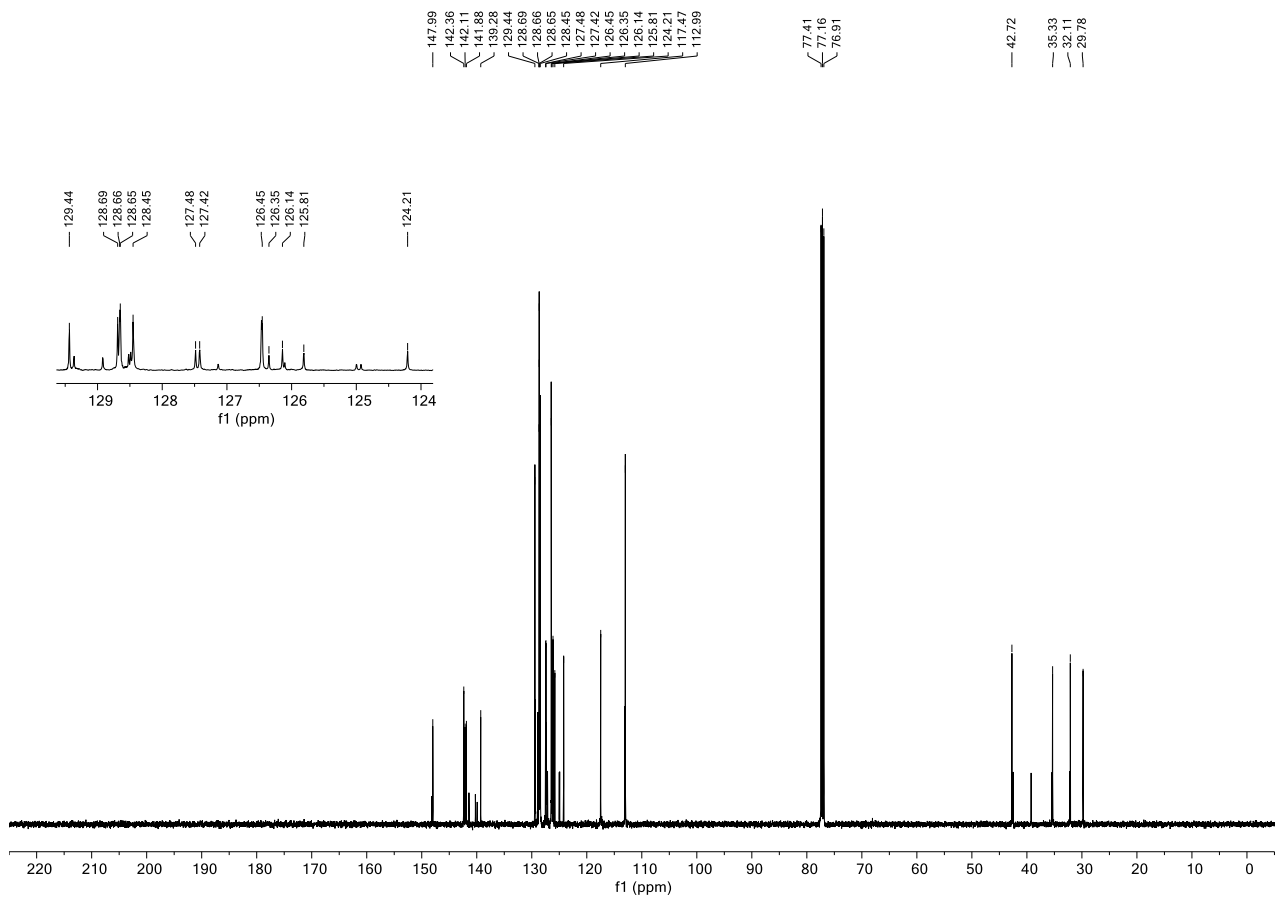
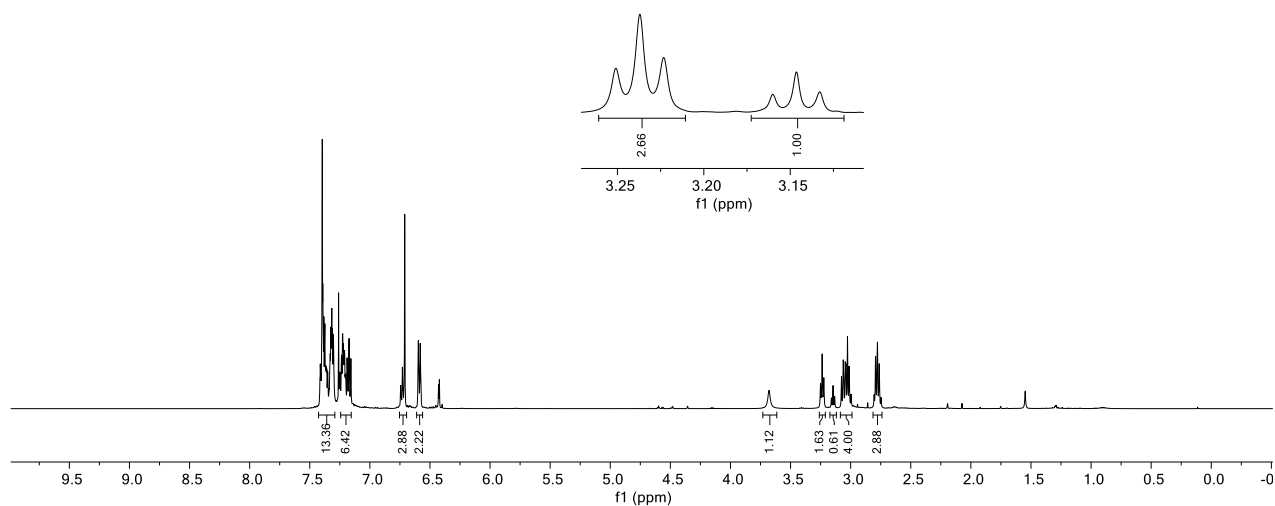
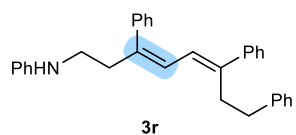


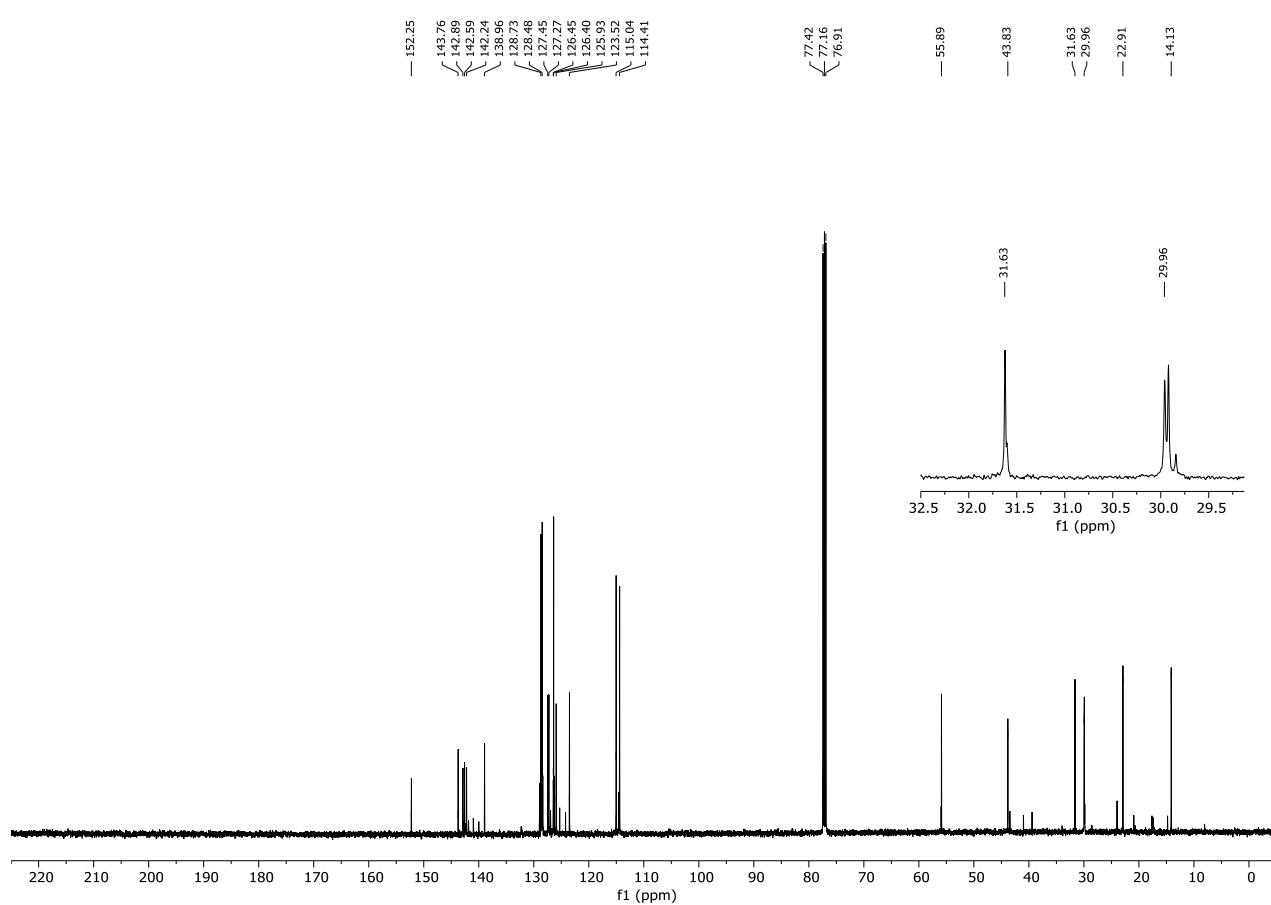
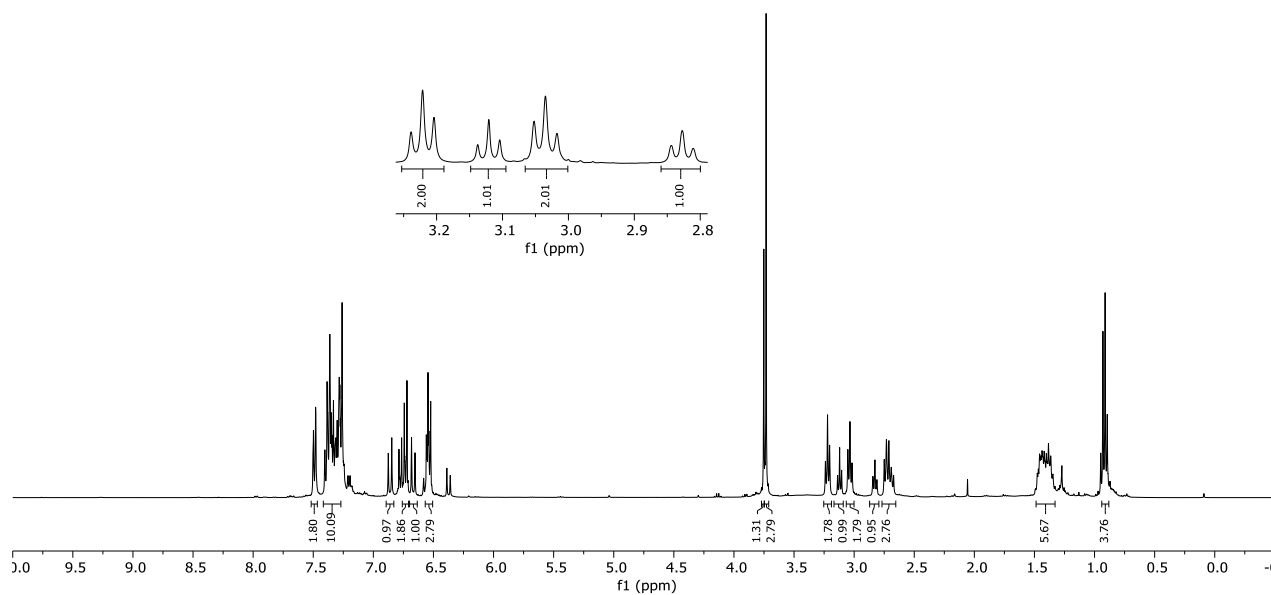
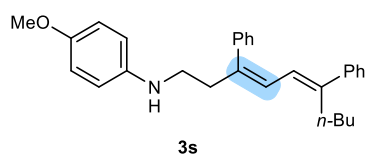
10.1:1 mixture of *E/Z* isomers

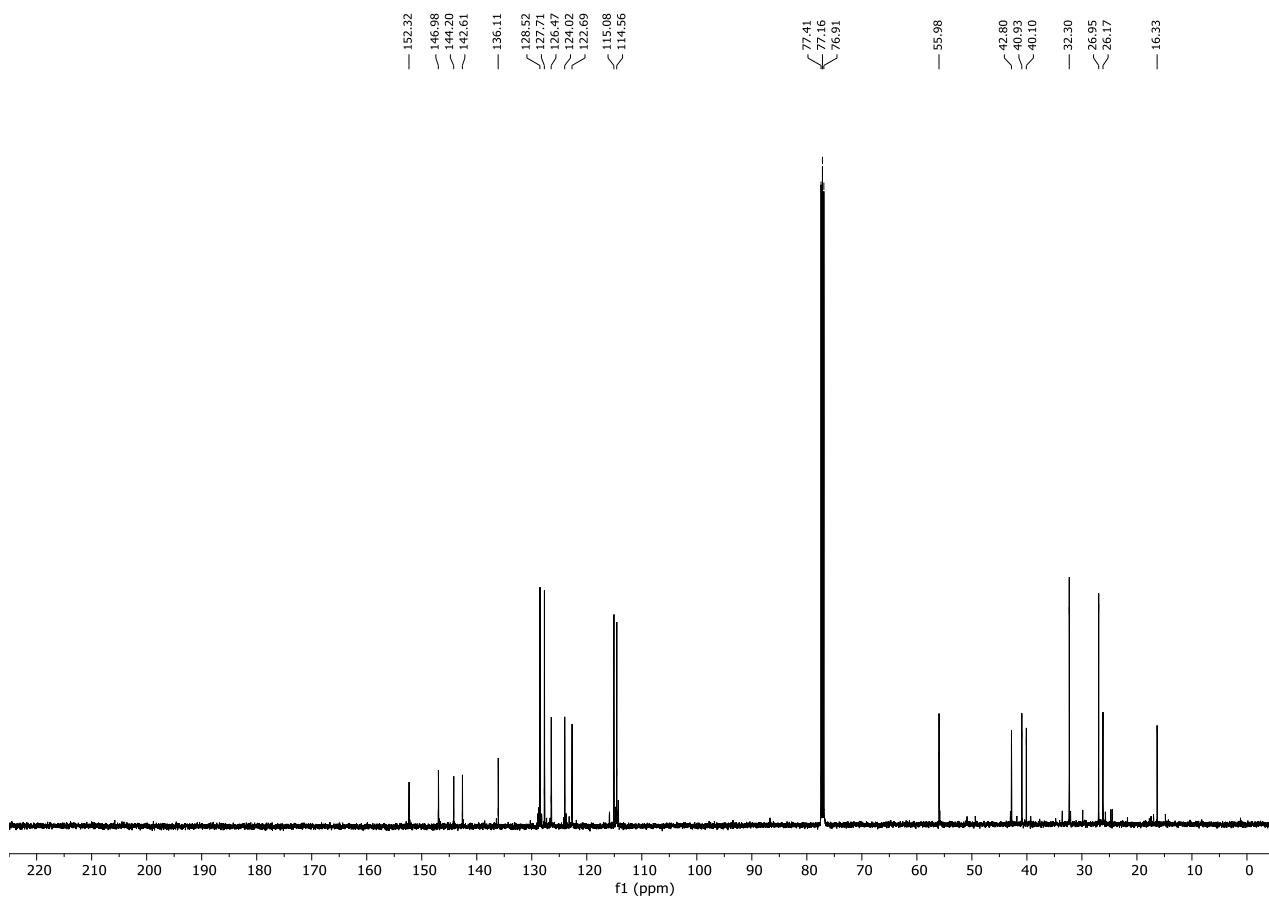
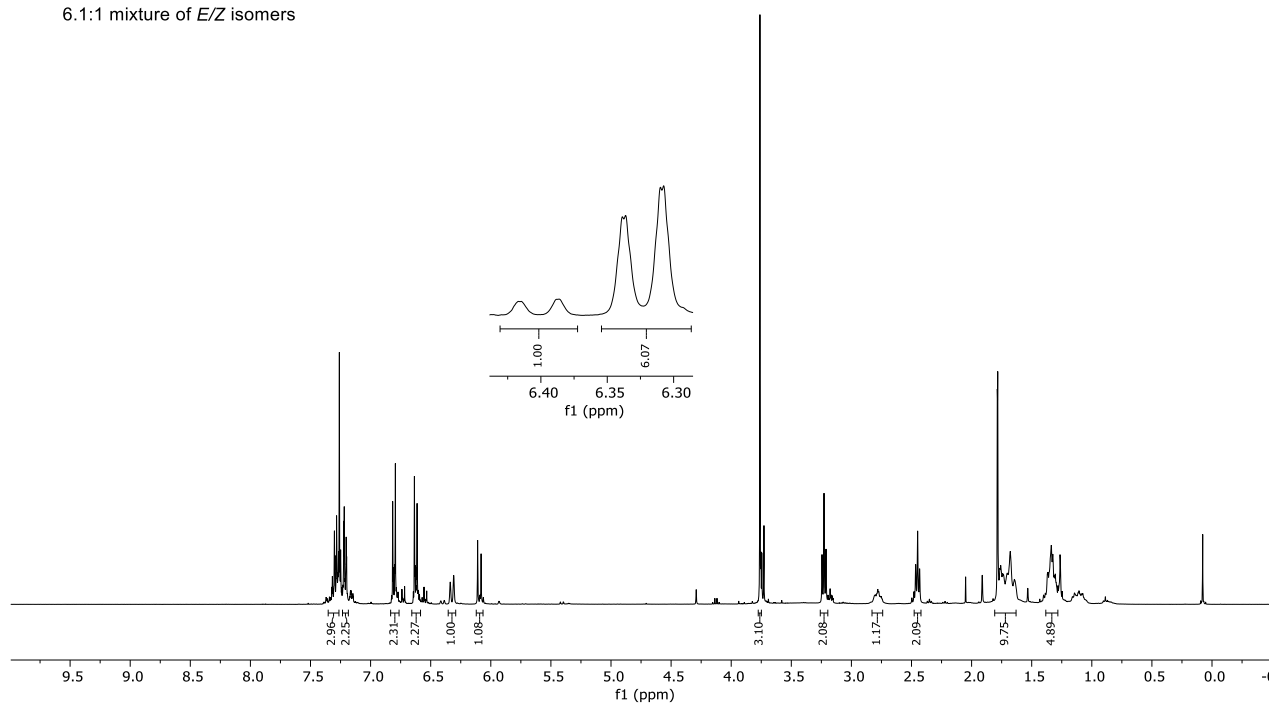
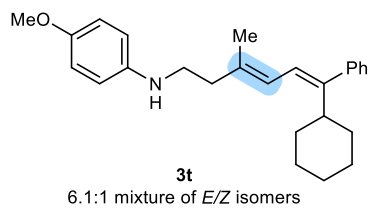


## NOESY Spectrum

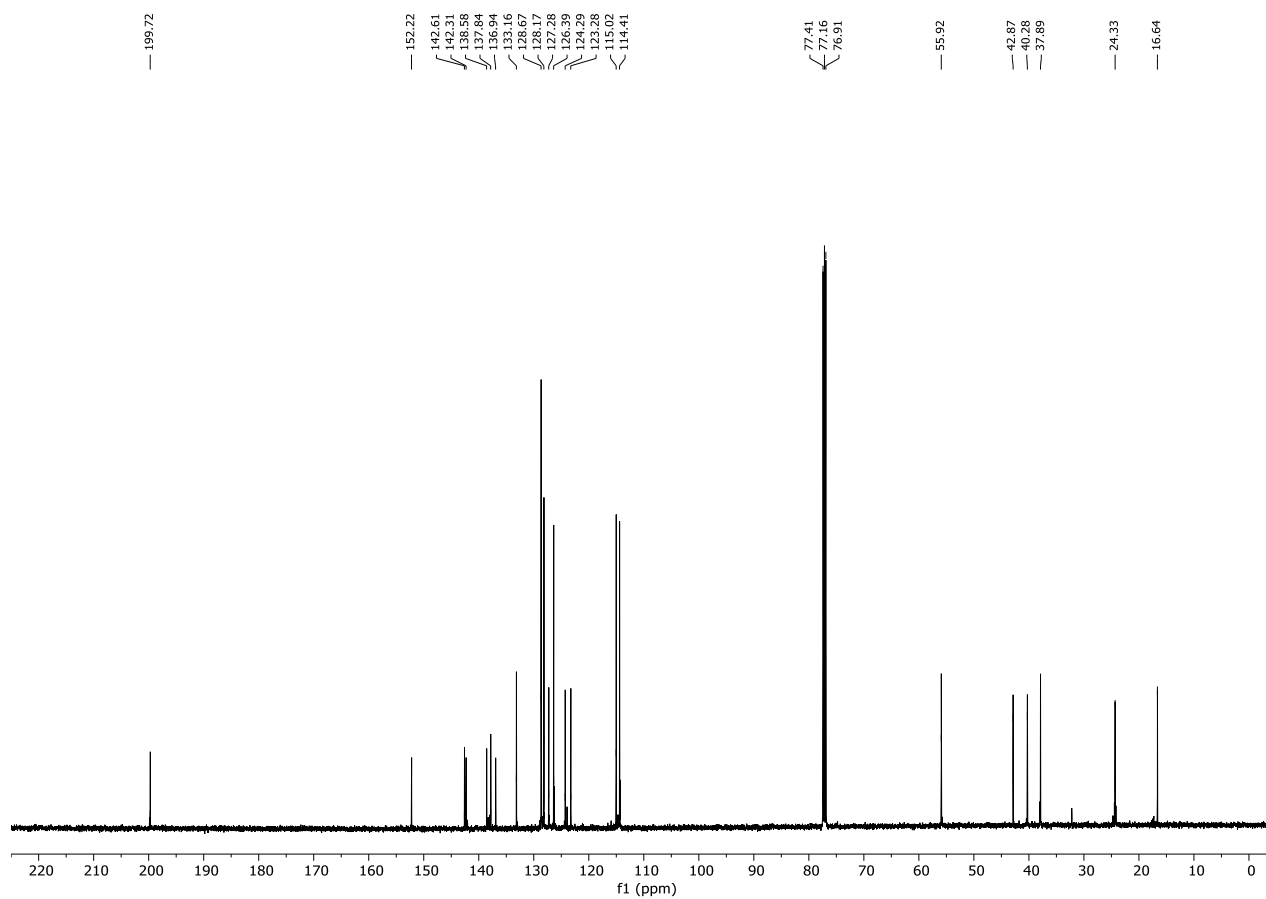
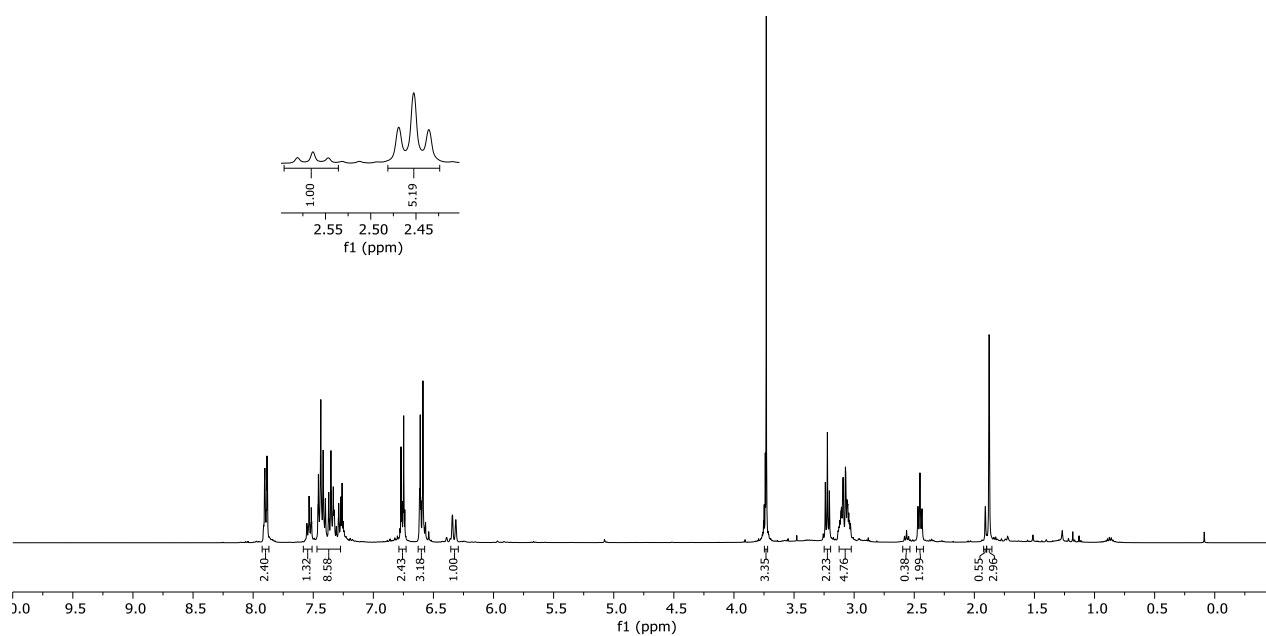
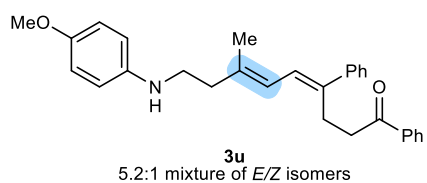


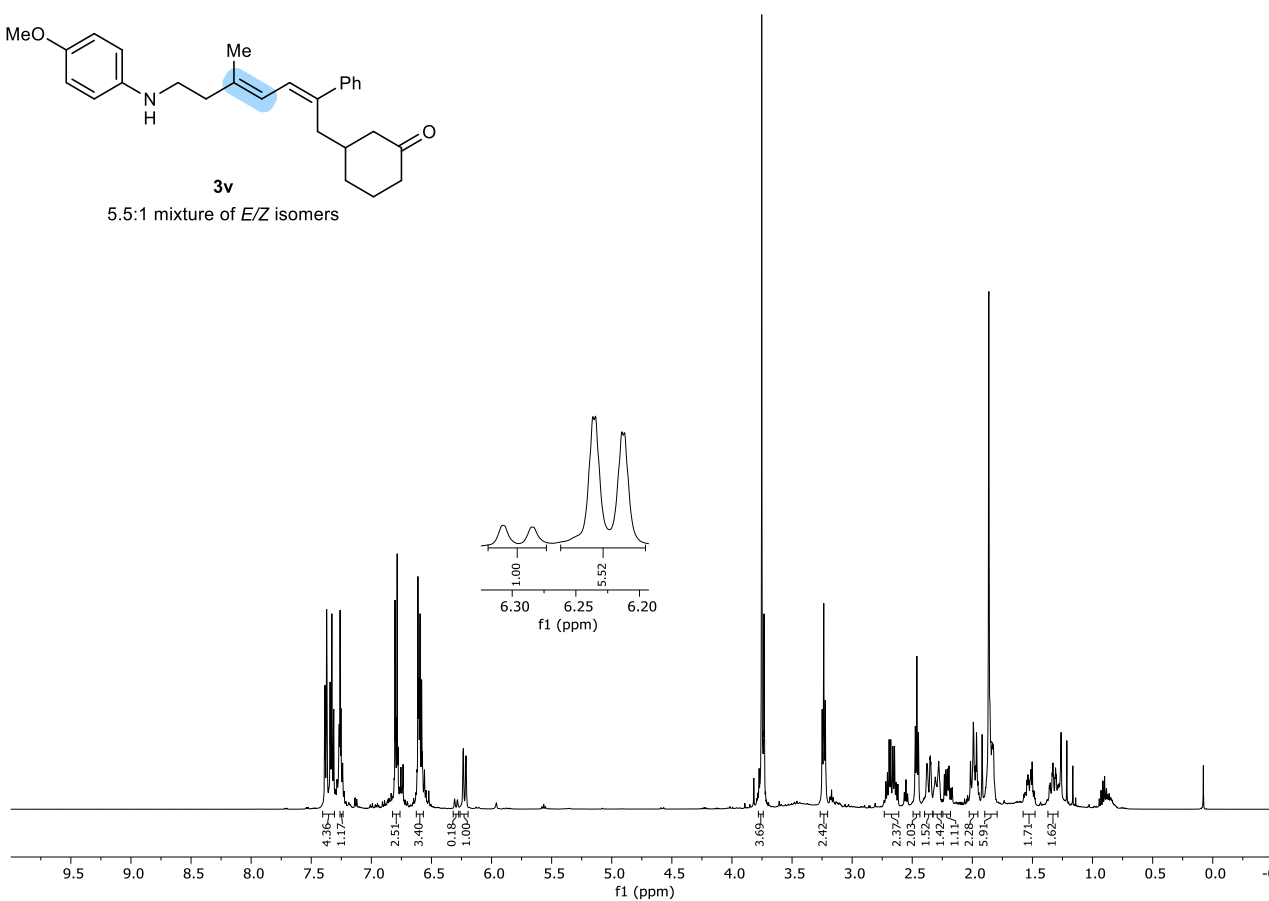
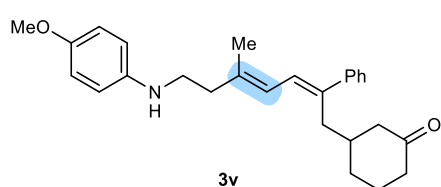




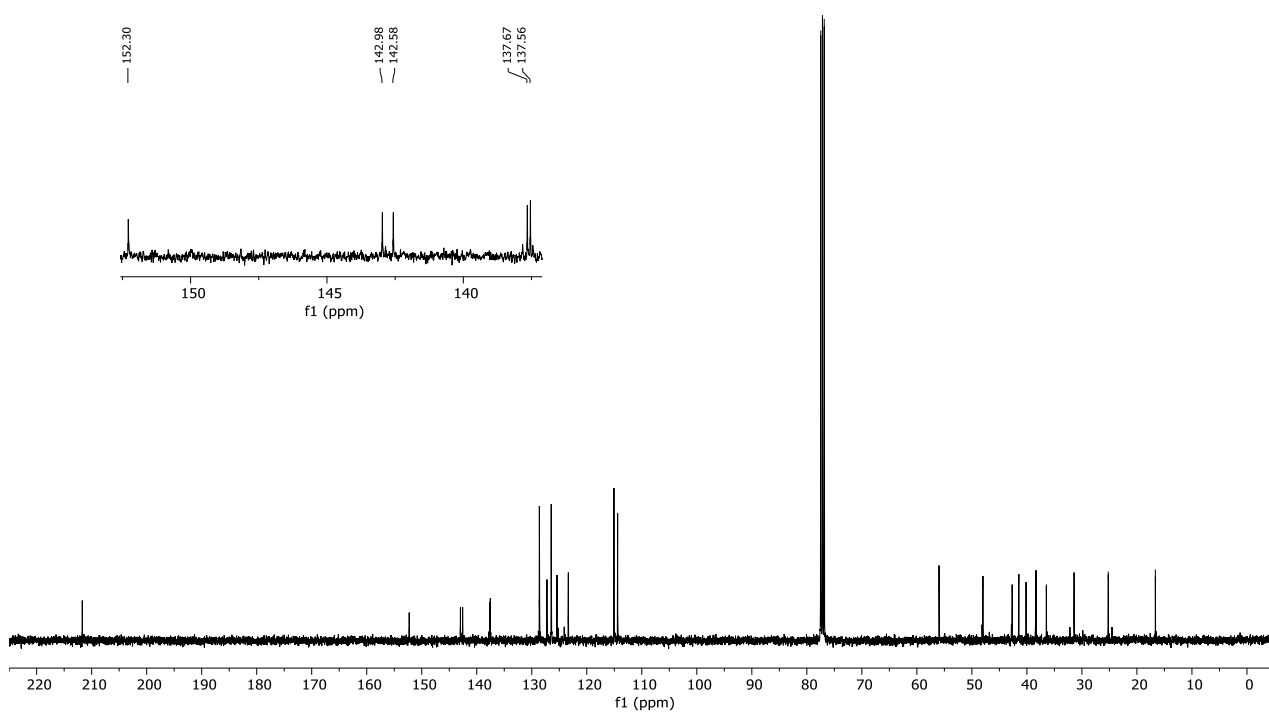








211.73  
152.30  
142.98  
142.58  
137.67  
137.56  
128.64  
127.25  
125.42  
123.37  
115.07  
114.40  
77.48  
77.16  
76.84  
55.98  
47.99  
42.68  
41.47  
40.15  
38.35  
36.46  
31.42  
25.21  
16.65



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