

Supporting Information for:

**Synthesis of nitrodienes, nitrostyrenes, and nitrobiaryls through palladium-catalyzed couplings of  $\beta$ -nitrovinyl and *o*-nitroaryl thioethers**

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**1. General Information**

All reactions were performed under Ar atmospheres with dry solvents in flame-dried reaction vessels containing Teflon stirrer bars. Toluene, acetonitrile, benzene, dichloromethane, and 1,2-



dichloroethane were distilled afresh from CaH<sub>2</sub> under a positive pressure of argon; MeOH was distilled from Mg<sup>0</sup> under a positive pressure of argon; THF was distilled afresh from Na<sup>0</sup> with benzophenone as indicator under a positive pressure of argon; triethyl phosphite was distilled from Na<sup>0</sup> under a positive pressure of argon and stored over activated 4-Å molecular sieves; triisopropyl borate was distilled from Na<sup>0</sup> under a positive pressure of argon immediately prior to use. *N,N*-Dimethylformamide was purchased in anhydrous grade from Sigma–Aldrich and used directly. Tetrakis(triphenylphosphine)palladium (0) was purchased from Strem Chemicals. Copper(I) thiophene-2-carboxylate (CuTC) was prepared according to a literature procedure.<sup>1</sup> Copper(I) diphenylphosphinate (CuDPP) was purchased from Synthonix and stored in a glove box under an argon atmosphere. (*E*)-Hexenylboronic acid (**2a**)<sup>2</sup> and (*E*)-3-hydroxypropenylboronic acid (**2n**)<sup>3</sup> were prepared according to literature procedures. Phenylboronic acid (**2b**), 3-bromophenylboronic acid (**2d**), 3,4-methylenedioxyphenylboronic acid (**2e**), 3-trifluoromethylphenylboronic acid (**2f**), 3-hydroxyphenylboronic acid (**2g**), pyridine-3-boronic acid (**2k**), and 2-methylphenylboronic acid (**2l**) were purchased from Combi-Blocks and used directly. 1-Phenylvinylboronic acid (**2i**) was purchased from Combi-Blocks and recrystallized from degassed H<sub>2</sub>O prior to use. 4-Chlorophenylboronic acid (**2c**) and *trans*-2-phenylvinylboronic acid (**2h**) were purchased from Sigma–Aldrich and used directly. All other reagents were used as received from commercial sources unless otherwise noted. Reactions were monitored using thin layer chromatography (TLC) performed on 0.25-mm Silicycle Glass-Backed Extra-Hard-Layer, 60-Å silica gel plates (TLG-R10011B-323) and visualized under UV light or through permanganate and anisaldehyde staining. Flash column chromatography was

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<sup>1</sup> Prokopcová, H.; Kappe, C. O. *J. Org. Chem.* **2007**, *72*, 4440.

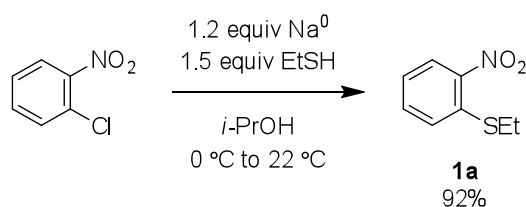
<sup>2</sup> Fairlamb, I. J. S.; Marrison, L. R.; Dickinson, J. M.; Lu, F.-J.; Schmidt, J. P. *Bioorg. Med. Chem.* **2004**, *12*, 4285.

<sup>3</sup> Clarke, P. A.; Rolla, G. A.; Cridland, A. P.; Gill, A. A. *Tetrahedron* **2007**, *63*, 9124.

performed using Silicycle SiliaFlash® P60 (230–400 mesh, R12030B) and compressed air. IR spectra were recorded using a Thermo Nicolet Avatar 370 FT-IR spectrometer. NMR spectra were recorded using a Bruker Avance-500 spectrometer, calibrated with as the solvent as the internal reference [7.26 (residual CHCl<sub>3</sub>) and 77.16 (CDCl<sub>3</sub>) ppm for <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively]. <sup>1</sup>H NMR spectral data are reported as follows: chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. <sup>13</sup>C NMR spectral data are reported in terms of the chemical shift (δ, ppm), followed by multiplicity and coupling constant in the case of C–F coupling. The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; br = broad. Mass spectra were recorded using an Applied Biosystems Voyager-DE STR MALDI-TOF spectrometer, in a reflector mode, under positive polarity. The accelerating voltage was 20,000 V, with a 350-ns extraction delay time. The matrix, 2,5-dihydrobenzoic acid, was also used as the internal calibrant (peaks at *m/z* 137.02 and 177.02). Data were analyzed using the instrument-supplied software. Additional GC-MS data were obtained using an Agilent 6890-5975 GC-MS equipped with an autosampler and a (5%-phenyl)-methylpolysiloxane HP-5 column.

## 2. Experimental Procedures

### 2.A. Preparation of Aryl Thioether **1a** and Vinyl Thioethers **1b–1d**

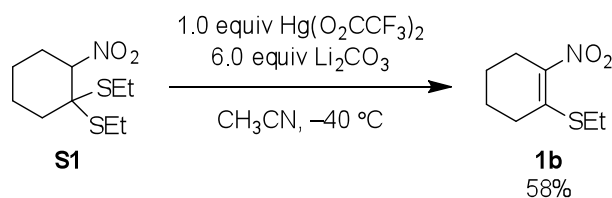


**1-Ethylthio-2-nitrobenzene (1a).** Prepared by adaptation of an analogous literature procedure for related compounds.<sup>4</sup> Cleaned, finely divided sodium metal (55 mg, 2.4 mmol, 1.2 equiv) was added to a flame-dried round-bottom flask, which was then vacuum-replenished with argon. Isopropanol (stored over activated molecular sieves for 1 h, 25 mL) was added directly to this flask, followed by ethanethiol (225  $\mu$ L, 3 mmol, 1.5 equiv). The solution was subsequently stirred until the sodium metal was consumed, typically 3 h. The flask was cooled to 0 °C and then a solution of 1-chloro-2-nitrobenzene (315 mg, 2 mmol, 1 equiv) in isopropanol (4 mL) was added dropwise over 1 min. The mixture was warmed slowly to 22 °C over 2 h, with the reaction's progress monitored by TLC (hexanes:EtOAc, 4:1; product spot slightly below that of the starting material;  $R_f$  = ca. 0.45); consumption of chlorobenzene was complete within 18 h. The reaction mixture was poured into a separatory funnel containing 0.2 M hydrochloric acid (20 mL) and EtOAc (40 mL) and then the layers were separated. The organic layer was further washed with water (20 mL) and brine (20 mL). The combined aqueous layers were back-extracted with EtOAc (20 mL) and the combined organic layers subsequently dried ( $MgSO_4$ ). After filtering, the volatiles were evaporated in vacuo and the crude oil loaded onto a silica gel column and purified through flash chromatography (gradient, 2–4% EtOAc in hexanes). Product **1a** was isolated as a yellow oil (336 mg, 92%). NOTE: On a larger scale, purification of the crude, concentrated reaction mixture following extraction was conveniently performed via distillation, with a head temperature of 120 °C at ca. 1 mm Hg. Spectroscopic characteristics were identical to those reported previously.<sup>5</sup>

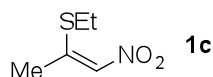
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<sup>4</sup> a) Montanari, S.; Paradisi, C.; Scorrano, G. *J. Org. Chem.* **1991**, *56*, 4274. b) Foster, D. G.; Reid, E. E. *J. Am. Chem. Soc.* **1924**, *46*, 1936.

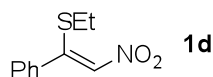
<sup>5</sup> Duan, Z.; Ranjit, S.; Zhang, P.; Liu, X. *Chem. Eur. J.* **2009**, *15*, 3666.



**1-Ethylthio-2-nitrocyclohex-1-ene (1b).** The dithioacetal **S1** was prepared according to literature procedures.<sup>6</sup> Dithioacetal elimination was performed according to an alternative literature procedure.<sup>7</sup> A dry, argon-replenished round-bottom flask was charged with mercury(II) trifluoroacetate (4.26 g, 10.0 mmol, 1.0 equiv) and lithium carbonate (4.43 g, 60.0 mmol, 6.0 equiv), which were suspended in dry acetonitrile (60 mL) and cooled to  $-40\text{ }^\circ\text{C}$ . The dithioacetal **S1** (2.49 g, 10.0 mmol, 1.0 equiv) was added dropwise over 1 min to the white suspension. The reaction's progress was monitored by TLC (hexanes:EtOAc, 4:1; product  $R_f = 0.35$ ), with the starting material consumed within 1 h. The reaction was quenched with the addition of EtOAc (100 mL) and water (100 mL). After filtration, the biphasic mixture was separated and the organic layer further washed with water (100 mL), dried ( $\text{MgSO}_4$ ), and concentrated. The crude reaction product was recrystallized ( $\text{Et}_2\text{O}$ ) to yield as bright yellow needles (1.09 g, 58%). Spectroscopic characteristics were identical to those reported previously.<sup>6</sup>



**(Z)-2-Ethylthio-1-nitro-1-propene (1c).** Prepared according to literature procedures.<sup>6</sup> Spectroscopic characteristics were identical to those reported previously.

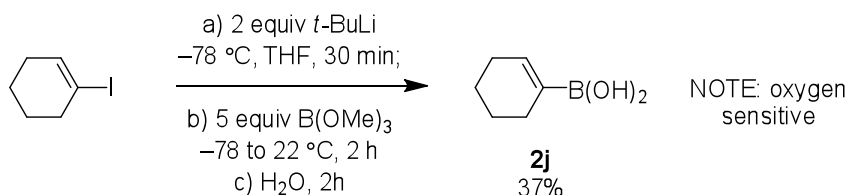


<sup>6</sup> Node, M.; Kawabata, T.; Fujimoto, M.; Fuji, K. *Synthesis* **1984**, 234.

<sup>7</sup> Jung, M. E.; Grove, D. D. *J. Chem. Soc., Chem. Commun.* **1987**, 753.

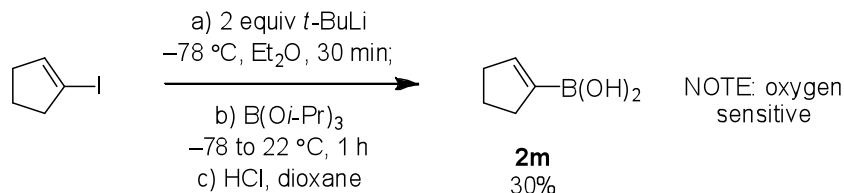
**(Z)-1-Ethylthio-2-nitro-2-phenylethene (1d)**. Prepared according to literature procedures.<sup>6</sup>  
Spectroscopic characteristics were identical to those reported previously.

## 2.B. Preparation of the Boronic acids **2j** and **2m**



**Cyclohexenylboronic acid (2j)**. Procedure adapted from a similar literature process.<sup>8</sup>  
Tetrahydrofuran (20 mL) and 1-iodocyclohexene (624 mg, 3.00 mmol, 1.0 equiv) were added to a dry, argon-replenished round-bottom flask equipped with a Teflon stirrer bar. The solution was cooled in a  $-78\text{ }^{\circ}\text{C}$  bath and then *tert*-butyllithium (1.4 M in pentane, 4.29 mL, 2.0 equiv) was added dropwise over 5 min. The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for an additional 30 min and then trimethyl borate (1.67 mL, 15.0 mmol, 5.0 equiv) was added dropwise over 1 min. The reaction flask was warmed to ambient temperature ( $22\text{ }^{\circ}\text{C}$ ) over 30 min and then the mixture was stirred for an additional 2 h. Water (5 mL) was added and then the mixture was stirred for 2 h. The aqueous reaction mixture was poured into a separatory funnel and extracted with  $\text{Et}_2\text{O}$  ( $3 \times 30$  mL). The combined organic phases were washed with 1 M HCl ( $2 \times 20$  mL) and dried ( $\text{Na}_2\text{SO}_4$ ). Following evaporation of the solvent under reduced pressure, the crude white solid was transferred to a round-bottom flask, equipped with a Teflon stirrer bar and condenser, which was subsequently argon-replenished. Under the argon atmosphere, the crude boronic acid was recrystallized from a minimal volume of degassed water (freeze–pump–thaw method), to provide white crystals (140 mg, 37%) that were used without further characterization.

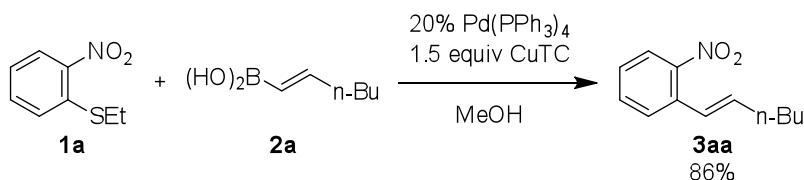
<sup>8</sup> Alvarez, R.; Domínguez, M.; Pazos, Y.; Sussman, F.; de Lera, A. R. *Chem. Eur. J.* **2003**, *9*, 5821.



**Cyclopentenylboronic acid (2m).** Et<sub>2</sub>O (40 mL) and 1-iodocyclopentene (3.0 g, 15.46 mmol, 1.0 equiv) were added to a dry, argon-replenished round-bottom flask equipped with a Teflon stirrer bar. The solution was cooled in a -78 °C bath and then *t*-BuLi (1.4 M in pentane, 22.0 mL, 2.0 equiv) was added dropwise over 5 min. The reaction mixture was stirred at -78 °C for an additional 30 min and then a solution of triisopropylborate (3.57 mL, 15.46 mmol, 1.0 equiv) in Et<sub>2</sub>O (20 mL) was added dropwise over 5 min. The mixture was stirred at -78 °C for 1 h, before being warmed to room temperature over 30 min and then stirred at ambient temperature for an additional 30 min. The reaction was quenched with an anhydrous solution of hydrogen chloride (4.0 M in dioxane, 7.73 mL, 2 equiv), followed by the addition of water (2.78 mL, 154.6 mmol, 10 equiv), and then the mixture was stirred for an additional 2 h. The reaction mixture was poured into a separatory funnel and washed with water (20 mL); the aqueous phase was then extracted further with Et<sub>2</sub>O (2 × 10 mL). After evaporation of the combined organic solvents under reduced pressure, the crude white solid was transferred to a round-bottom flask, equipped with a Teflon stirrer bar and condenser, which was subsequently argon-replenished. Under the argon atmosphere, the crude boronic acid was recrystallized from a minimal volume of degassed water (freeze-pump-thaw method), providing white crystals (518 mg, 30%) that were used without further characterization.

## 2.C. Thioether Cross-Coupling with Boronic Acids

### Representative procedure

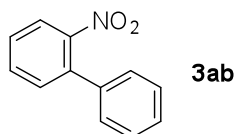


**(E)-2-(Hex-1-enyl)-1-nitrobenzene (3aa).** A dry, argon-replenished reaction vessel was charged with copper(I) thiophene carboxylate (46 mg, 0.24 mmol, 1.5 equiv), hexenylboronic acid (**2a**, 61 mg, 0.48 mmol, 3.0 equiv), and palladium tetrakis(triphenylphosphine) (37 mg, 0.032 mmol, 0.20 equiv). NOTE: In the case of the vinyl thioethers **1b-d**, the loading of palladium tetrakis(triphenylphosphine) was 0.10 equiv. The solid mixture was vacuum-replenished with argon prior to the addition of a solution of aryl thioether **1a** (29.3 mg, 0.160 mmol, 1.0 equiv) in distilled methanol (6 mL). The solution was stirred under a positive pressure of argon at 22 °C; it turned from red/yellow to dark brown within ca. 2 min. The reaction's progress was monitored by TLC (hexanes:EtOAc, 4:1; product  $R_f = 0.7$ ), with complete consumption of the starting thioether typically within 2 h. The reaction was quenched through the addition of EtOAc (20 mL) and saturated ammonium chloride (15 mL); the layers were separated and the organic phase washed successively with water (15 mL) and brine (2 × 15 mL). The combined aqueous layers were then back-extracted with EtOAc (10 mL); the combined organic layers were dried (MgSO<sub>4</sub>). After evaporation of the solvent under reduced pressure, the crude residue was loaded onto a silica gel column and purified through flash chromatography (hexanes/benzene/EtOAc, gradient from 89:10:1 to 84:10:6) to yield a light yellow oil (28.2 mg, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.86 (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.58 (dd,  $J = 7.9, 1.2$  Hz, 1H), 7.52 (td,  $J = 7.8, 0.9$  Hz, 1H), 7.33 (td,  $J = 7.8, 1.4$  Hz, 1H), 6.83 (d,  $J = 15.6$  Hz, 1H), 6.24 (dt,  $J = 15.6, 7.0$  Hz, 1H),

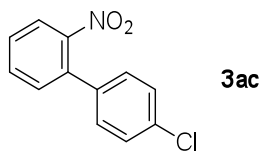


2.27 (qd,  $J = 7.2, 1.3$  Hz, 2H), 1.51–1.45 (m, 2H), 1.43–1.37 (m, 2H), 0.94 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.7, 136.9, 133.4, 132.7, 128.4, 127.3, 124.8, 124.3, 32.8, 31.1, 22.2, 13.9; IR (film)  $\nu_{\text{max}}$  2958, 2929, 2872, 1605, 1520, 1352, 960, 788  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{12}\text{H}_{15}\text{NO}_2$  [M]  $m/z$  205.1, found 205.1.

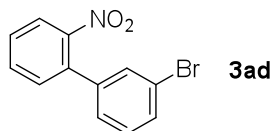
### 2.C.i. Physical and Spectroscopic Data for the Nitroorganics 3



**2-Nitrobiphenyl (3ab).** 99% yield; light-yellow oil. Spectroscopic characteristics were identical to those reported previously.<sup>9</sup>



**1-(4-Chlorophenyl)-2-nitrobenzene (3ac).** 96% yield; light-yellow oil. Spectroscopic characteristics were identical to those reported previously.<sup>10</sup>

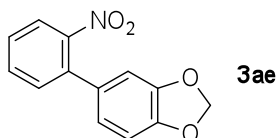


**1-(3-Bromophenyl)-2-nitrobenzene (3ad).** 94% yield; light-yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.91 (dd,  $J = 8.1, 1.2$  Hz, 1H), 7.64 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.55–7.51 (m, 2H), 7.49 (t,

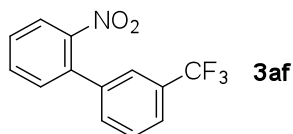
<sup>9</sup> Desmarets, C.; Omar-Amrani, R.; Walcarius, A.; Lambert, J.; Champagne, B.; Fort, Y.; Schneider, R. *Tetrahedron* **2008**, *64*, 372.

<sup>10</sup> Felpin, F.-X.; Fouquet, E.; Zakri, C. *Adv. Synth. Catal.* **2009**, *351*, 649.

$J = 1.7$  Hz, 1H), 7.41 (dd,  $J = 7.7, 1.3$  Hz, 1H), 7.29 (t,  $J = 7.8$  Hz, 1H), 7.24 (ddd,  $J = 7.7, 1.5, 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.9, 139.5, 134.9, 132.5, 131.9, 131.2, 130.9, 130.1, 128.7, 126.6, 124.3, 122.6; IR (film)  $\nu_{\text{max}}$  3061, 2856, 1596, 1520, 1351, 855, 780, 750  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{12}\text{H}_8\text{NO}_2\text{Br}$  [M]  $m/z$  277.0, found 277.0.

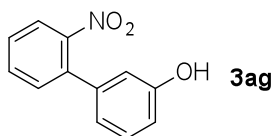


**1-(3,4-Methylenedioxyphenyl)-2-nitrobenzene (3ae).** 99% yield; light-yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.80 (dd,  $J = 8.0, 0.9$  Hz, 1H), 7.58 (td,  $J = 7.6, 1.1$  Hz, 1H), 7.45 (td,  $J = 7.9, 1.2$  Hz, 1H), 7.42 (dd,  $J = 7.7, 1.2$  Hz, 1H), 6.86 (d,  $J = 7.9$  Hz, 1H), 6.80 (d,  $J = 1.7$  Hz, 1H), 6.77 (dd,  $J = 7.9, 1.8$  Hz, 1H), 6.01 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  149.4, 147.9, 147.8, 135.8, 132.1, 131.9, 130.9, 127.9, 124.0, 121.6, 108.6, 108.5, 101.4; IR (film)  $\nu_{\text{max}}$  2891, 2781, 1602, 1567, 1526, 1479, 1351, 1217  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{13}\text{H}_{10}\text{NO}_4$  [M + H] $^+$   $m/z$  244.060, found 244.057.

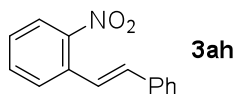


**2-Nitro-1-(3-trifluoromethylphenyl)benzene (3af).** 88% yield; light-yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.96 (dd,  $J = 8.1, 1.2$  Hz, 1H), 7.67 (td,  $J = 7.6, 1.2$  Hz, 2H), 7.60 (s, 1H), 7.57–7.54 (m, 2H), 7.49 (d,  $J = 7.8$  Hz, 1H), 7.44 (dd,  $J = 7.6, 1.4$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.8, 138.3, 135.0, 132.6, 131.9, 131.2, 131.0 (q,  $J_{\text{CF}} = 32.4$  Hz), 128.9, 128.8, 124.9 (q,  $J_{\text{CF}} = 4.2$  Hz), 124.7 (q,  $J_{\text{CF}} = 3.5$  Hz), 124.3, 123.4 (q,  $J_{\text{CF}} = 246.2$  Hz); IR (film)  $\nu_{\text{max}}$

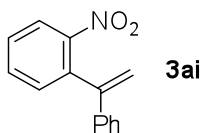
3078, 2868, 1602, 1561, 1514, 1339, 1170, 1124  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{13}\text{H}_8\text{NO}_2\text{F}_3$  [M]  
 $m/z$  267.1, found 267.1.



**1-(3-Hydroxyphenyl)-2-nitrobenzene (3ag).** 91% yield. Spectroscopic characteristics were identical to those reported previously.<sup>11</sup>



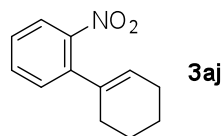
**(E)-1-Nitro-2-styrylbenzene (3ah).** 99% yield. Spectroscopic characteristics were identical to those reported previously.<sup>12</sup>



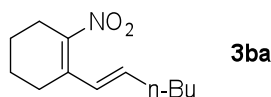
**1-Nitro-2-(1-phenylvinyl)benzene (3ai).** 53% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.99 (dd,  $J$  = 8.2, 1.2 Hz, 1H), 7.68 (td,  $J$  = 7.6, 1.3 Hz, 1H), 7.56 (ddd,  $J$  = 8.2, 7.5, 1.5 Hz, 1H), 7.51 (dd,  $J$  = 7.6, 1.4 Hz, 1H), 7.34–7.31 (m, 3H), 7.30–7.27 (m, 2H), 5.80 (d,  $J$  = 0.4 Hz, 1H), 5.37 (d,  $J$  = 0.4 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.8, 146.3, 139.0, 136.8, 132.7, 132.3, 128.5, 128.3, 128.0, 126.4, 124.2, 115.4; IR (film)  $\nu_{\text{max}}$  3055, 2909, 2851, 1520, 1351, 908, 773, 703  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{14}\text{H}_{12}\text{NO}_2$  [M + H]<sup>+</sup>  $m/z$  226.09, found 226.08.

<sup>11</sup> Gustafson, J. L.; Lim, D.; Miller, S. J. *Science* **2010**, 328, 1251.

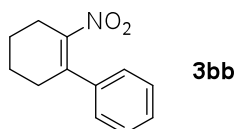
<sup>12</sup> Sore, H. F.; Boehner, C. M.; MacDonald, S. J. F.; Norton, D.; Fox, D. J.; Spring, D. R. *Org. Biomol. Chem.* **2009**, 7, 1068.



**1-Nitro-2-(cyclohex-1-enyl)benzene (3aj).** 83% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.79 (d,  $J = 8.2$  Hz, 1H), 7.51 (td,  $J = 7.6, 1.1$  Hz, 1H), 7.35 (td,  $J = 7.2, 1.1$  Hz, 1H), 7.28 (dd,  $J = 7.7, 1.1$  Hz, 1H), 5.63 (t,  $J = 1.7$  Hz, 1H), 2.23 (br s, 2H), 2.15 (br s, 2H), 1.77 (p,  $J = 5.9$  Hz, 2H), 1.68 (p,  $J = 5.9$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.7, 139.5, 135.8, 132.3, 130.8, 127.3, 126.7, 123.8, 29.3, 25.4, 22.8, 21.7; IR (film)  $\nu_{\text{max}}$  2944, 2851, 2827, 1602, 1567, 1532, 1357, 738  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{12}\text{H}_{15}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$   $m/z$  204.102, found 204.105.

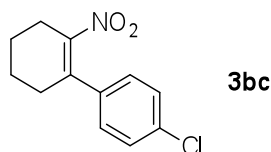


**(E)-1-(Hex-1-enyl)-2-nitrocyclohex-1-ene (3ba).** 86% yield. Spectroscopic characteristics were identical to those reported previously.<sup>13</sup>

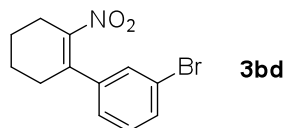


**1-Phenyl-2-nitrocyclohex-1-ene (3bb).** 99% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.37–7.29 (m, 3H), 7.16 (dd,  $J = 8.0, 1.3$  Hz, 2H), 2.71 (sept,  $J = 2.9$  Hz, 2H), 2.48 (sept,  $J = 2.9$  Hz, 2H), 1.90–1.85 (m, 2H), 1.82–1.76 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  146.7, 139.2, 139.0, 128.6, 128.0, 126.2, 32.3, 26.7, 22.0, 21.8; IR (film)  $\nu_{\text{max}}$  3056, 3019, 2942, 2864, 1945, 1520, 756, 690  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{12}\text{H}_{14}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$   $m/z$  204.10, found 204.07.

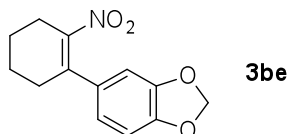
<sup>13</sup> Creech, G. S.; Kwon, O. *J. Am. Chem. Soc.* **2010**, *132*, 8876.



**1-(4-Chlorophenyl)-2-nitrocyclohex-1-ene (3bc).** 90% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.32 (d,  $J = 8.5$  Hz, 2H), 7.09 (d,  $J = 8.5$  Hz, 2H), 2.70 (sept,  $J = 2.9$  Hz, 2H), 2.44 (sept,  $J = 2.9$  Hz, 2H), 1.89–1.84 (m, 2H), 1.81–1.76 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.1, 138.1, 137.4, 134.0, 128.9, 127.7, 32.3, 26.6, 21.9, 21.7; IR (film)  $\nu_{\text{max}}$  2950, 2862, 1596, 1509, 1345, 1096, 1007, 826  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{Cl}$   $[\text{M} + \text{H}]^+$   $m/z$  238.07, found 238.05.

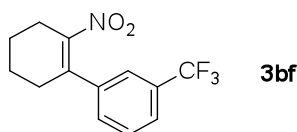


**1-(3-Bromophenyl)-2-nitrocyclohex-1-ene (3bd).** 99% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.43 (ddd,  $J = 8.1, 1.9, 1.0$  Hz, 1H), 7.30 (t,  $J = 1.8$  Hz, 1H), 7.21 (t,  $J = 7.9$  Hz, 1H), 7.07 (dt,  $J = 7.7, 1.2$  Hz, 1H), 2.70 (sept,  $J = 2.9$  Hz, 2H), 2.44 (sept,  $J = 2.9$  Hz, 2H), 1.89–1.83 (m, 2H), 1.80–1.75 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.1, 141.1, 138.1, 131.0, 130.1, 129.2, 125.0, 122.5, 32.4, 26.5, 21.9, 21.7; IR (film)  $\nu_{\text{max}}$  2950, 2868, 1511, 1344, 1152, 1070, 776, 690  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{12}\text{H}_{12}\text{NO}_2\text{Br}$   $[\text{M}]$   $m/z$  281.0, found 281.0.

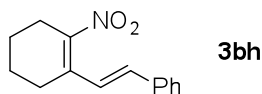


**1-(3,4-Methylenedioxyphenyl)-2-nitrocyclohex-1-ene (3be).** 99% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  6.76 (d,  $J = 8.0$  Hz, 1H), 6.64 (d,  $J = 1.5$  Hz, 1H), 6.61 (dd,  $J = 8.0, 1.6$  Hz, 1H), 5.96 (s, 2H), 2.67 (sept,  $J = 2.9$  Hz, 2H), 2.43 (sept,  $J = 2.9$  Hz, 2H), 1.87–1.82 (m, 2H), 1.79–1.73 (m,

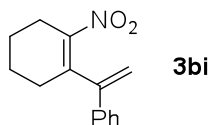
2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.8, 147.4, 146.8, 138.2, 132.4, 119.8, 108.5, 107.1, 101.2, 32.2, 26.8, 21.9, 21.8; IR (film)  $\nu_{\text{max}}$  2946, 1601, 1520, 1438, 1344, 1250, 1033, 805  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}_4$   $[\text{M} + \text{H}]^+$   $m/z$  248.092, found 248.085.



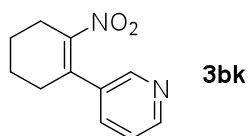
**1-(3-Trifluoromethylphenyl)-2-nitrocyclohex-1-ene (3bf).** 96% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.57 (d,  $J = 7.6$  Hz, 1H), 7.47 (t,  $J = 7.8$  Hz, 1H), 7.42 (s, 1H), 7.33 (d,  $J = 7.7$  Hz, 1H), 2.72 (sept,  $J = 2.9$  Hz, 2H), 2.48 (sept,  $J = 2.9$  Hz, 2H), 1.92–1.86 (m, 2H), 1.84–1.78 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.4, 139.9, 138.3, 131.0 (q,  $J_{\text{CF}} = 32.4$  Hz), 129.8, 129.1, 124.7 (q,  $J_{\text{CF}} = 3.7$  Hz), 123.8 (q,  $J_{\text{CF}} = 272.4$  Hz), 123.2 (q,  $J_{\text{CF}} = 3.8$  Hz), 32.5, 26.5, 21.9, 21.7; IR (film)  $\nu_{\text{max}}$  2946, 2868, 1659, 1516, 1328, 1123, 1070, 702  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{F}_3$   $[\text{M} + \text{H}]^+$   $m/z$  272.09, found 272.08.



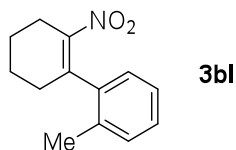
**(E)-1-(2-Phenylethenyl)-2-nitrocyclohex-1-ene (3bh).** 99% yield. Spectroscopic characteristics were identical to those reported previously.<sup>13</sup>



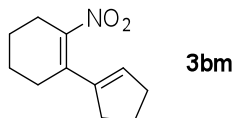
**1-(1-Phenylethenyl)-2-nitrocyclohex-1-ene (3bi).** 84% yield. Spectroscopic characteristics were identical to those reported previously.<sup>13</sup>



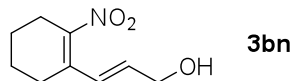
**1-(3-Pyridyl)-2-nitrocyclohex-1-ene (3bk).** 94% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.65 (br s, 1H), 8.56 (br s, 1H), 7.77 (d,  $J = 7.9$  Hz, 1H), 7.56 (t,  $J = 5.4$  Hz, 1H), 2.75 (sept,  $J = 2.8$  Hz, 2H), 2.49 (sept,  $J = 2.8$  Hz, 2H), 1.93–1.87 (m, 2H), 1.85–1.79 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.7, 145.1, 143.7, 137.8, 135.6, 124.74, 124.71, 32.7, 26.2, 21.6, 21.4; IR (film)  $\nu_{\text{max}}$  2949, 2868, 1658, 1519, 1413, 1347, 1327, 716  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$  [ $\text{M} + \text{H}$ ] $^+$   $m/z$  205.10, found 205.95.



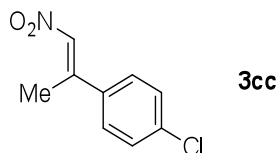
**1-(2-Methylphenyl)-2-nitrocyclohex-1-ene (3bl).** 81% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.23–7.12 (m, 3H), 6.97 (d,  $J = 7.2$  Hz, 1H), 2.83–2.66 (m, 2H), 2.45–2.31 (m, 2H), 2.23 (s, 3H), 1.89 (p,  $J = 6.1$  Hz, 2H), 1.78 (sept,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  146.5, 141.1, 138.9, 134.0, 130.0, 127.5, 126.0, 125.8, 32.6, 26.0, 22.1, 21.7, 19.0; IR (film)  $\nu_{\text{max}}$  2945, 2863, 1658, 1515, 1453, 1360, 1335, 753  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{13}\text{H}_{16}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$   $m/z$  218.12, found 218.11.



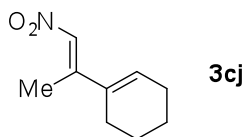
**1-(Cyclopent-1-enyl)-2-nitrocyclohex-1-ene (3bm).** 81% yield. Spectroscopic characteristics were identical to those reported previously.<sup>13</sup>



**1-(3-Hydroxyprop-1-enyl)-2-nitrocyclohex-1-ene (3bn).** 68% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  6.78 (d,  $J = 15.8$  Hz, 1H), 6.14 (dt,  $J = 15.8, 5.4$  Hz, 1H), 4.27 (d,  $J = 4.9$  Hz, 2H), 2.67–2.63 (m, 2H), 2.45–2.41 (m, 2H), 1.79–1.74 (m, 2H), 1.72–1.67 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.3, 134.0, 133.6, 125.6, 63.2, 27.1, 26.0, 21.9, 21.2; IR (film)  $\nu_{\text{max}}$  3357, 2941, 2868, 1506, 1343, 1323, 1091, 964  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{13}\text{H}_{16}\text{NO}_2$   $[\text{M} + \text{H}]^+$   $m/z$  184.10, found 184.12.



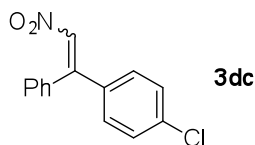
**(E)-2-(4-Chlorophenyl)-1-nitroprop-1-ene (3cc).** 90% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.42 (d,  $J = 8.9$  Hz, 2H), 7.39 (d,  $J = 8.9$  Hz, 2H), 7.28 (d,  $J = 1.4$  Hz, 1H), 2.62 (d,  $J = 1.4$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.4, 136.61, 136.60, 136.4, 129.3, 128.1, 18.4; IR (film)  $\nu_{\text{max}}$  3107, 2956, 2839, 1619, 1509, 1339, 1088, 820  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_9\text{H}_8\text{NO}_2\text{Cl}$   $[\text{M} + \text{H}]^+$   $m/z$  198.03, found 197.99.



**(E)-2-(Cyclohex-1-enyl)-1-nitroprop-1-ene (3cj).** 90% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.11 (s, 1H), 6.41 (t,  $J = 4.2$  Hz, 1H), 2.34 (d,  $J = 1.0$  Hz, 3H), 2.27–2.22 (m, 2H), 2.18–2.14 (m, 2H), 1.74–1.69 (m, 2H), 1.65–1.59 (2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  149.3, 134.8, 134.6,

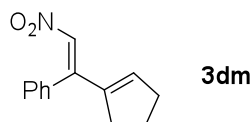


134.4, 26.5, 25.9, 22.4, 21.5, 14.8; IR (film)  $\nu_{\max}$  2932, 2851, 1625, 1590, 1514, 1328, 1234, 820  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_9\text{H}_{14}\text{NO}_2$   $[\text{M} + \text{H}]^+$   $m/z$  168.102, found 168.103.



mixture of diastereomers, ratio not determined

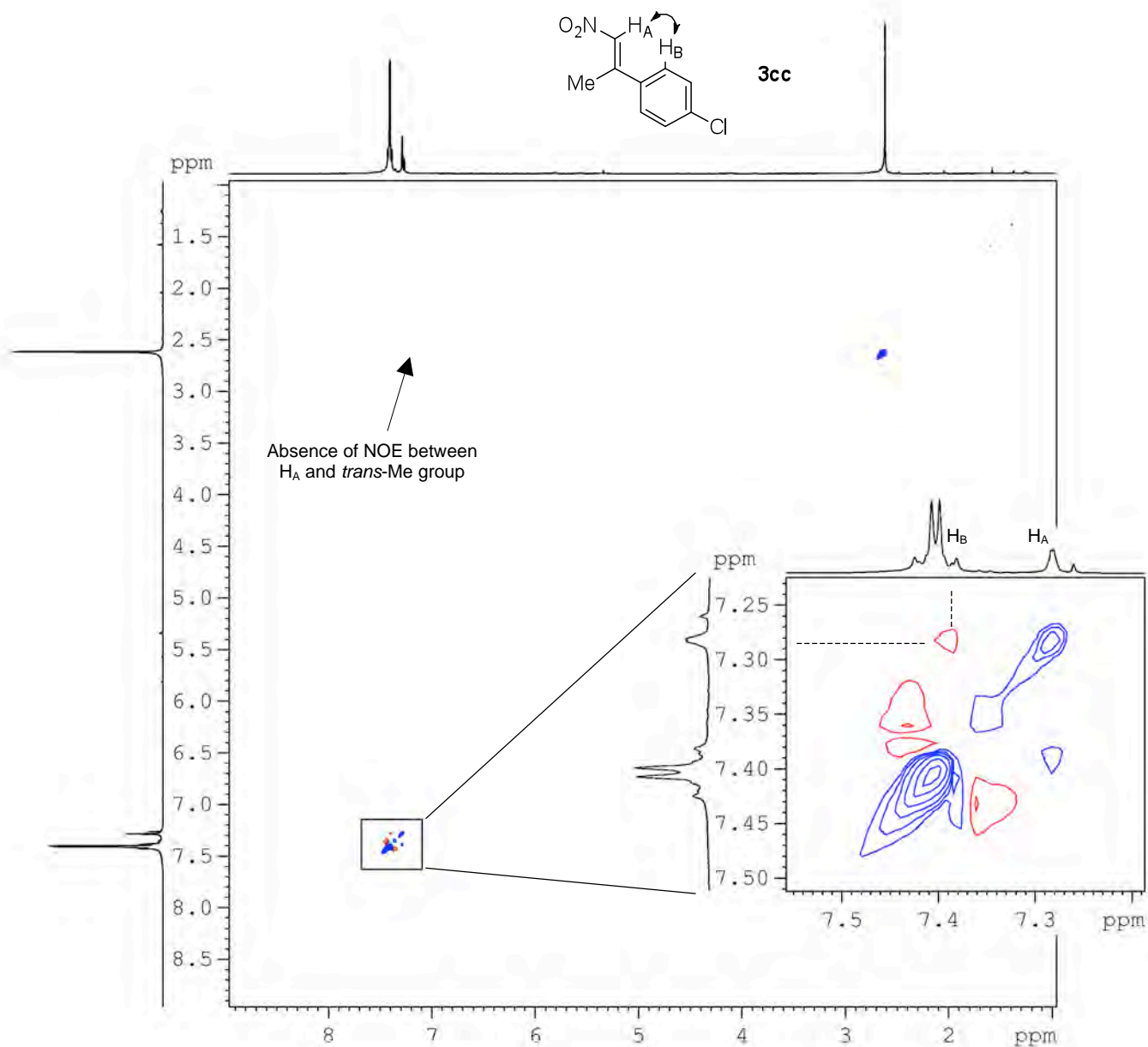
**(Z/E)-2-(4-Chlorophenyl)-2-phenyl-1-nitroethene (3dc).** 94% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.55–7.39 (m, 6H), 7.35–7.30 (m, 1H), 7.29–7.20 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  149.3, 149.1, 137.2, 136.6, 135.5, 135.0, 134.6, 134.4, 133.9, 131.1, 130.3, 130.1, 129.5, 129.2, 129.0, 128.84, 128.80, 128.71, 128.6; IR (film)  $\nu_{\max}$  3090, 2845, 1619, 1514, 1345, 1083, 820, 663  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{Cl}$   $[\text{M} + \text{H}]^+$   $m/z$  260.047, found 260.052.

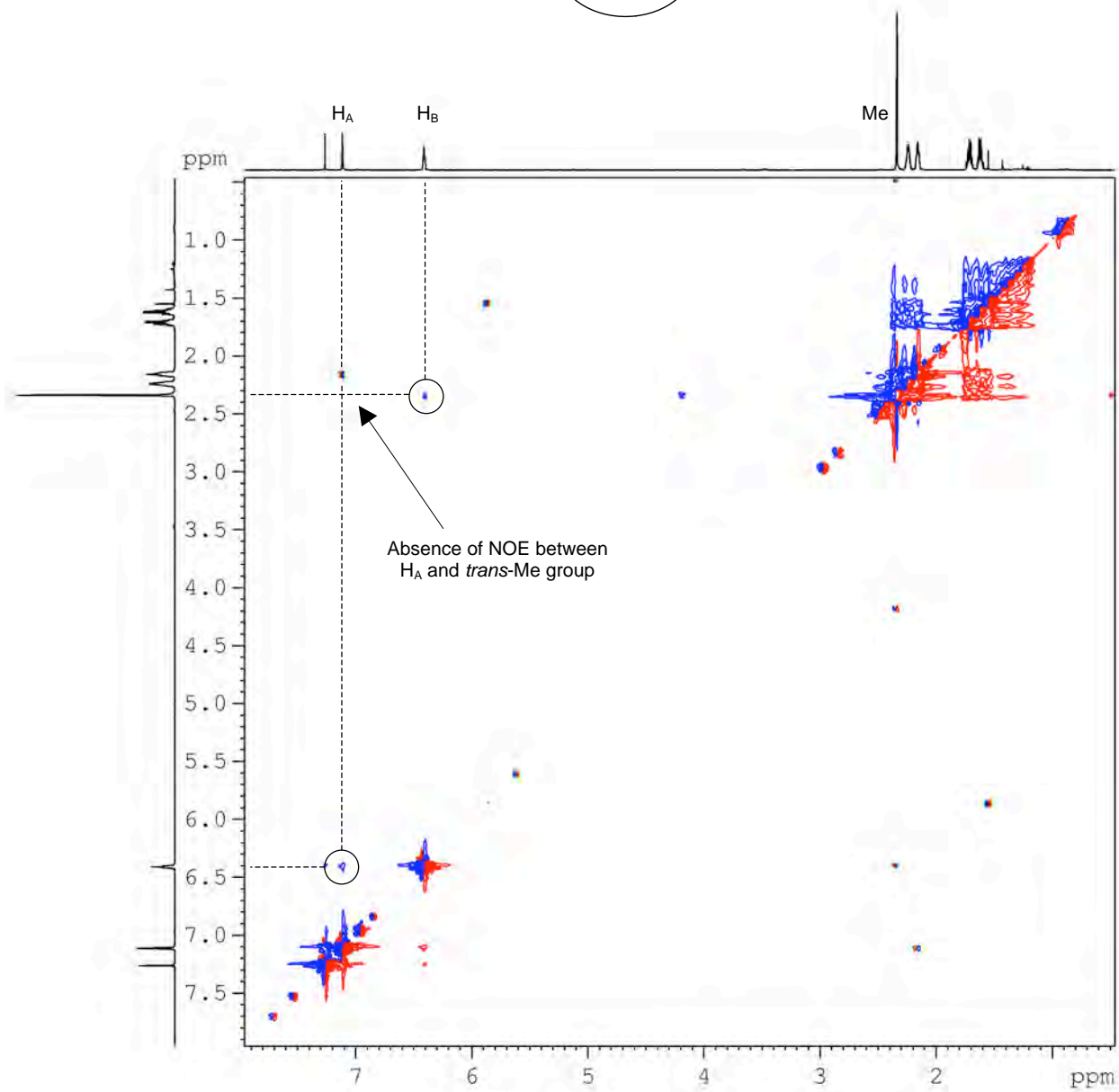
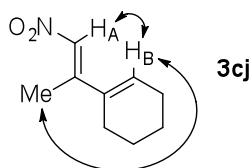


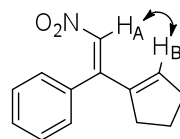
**(E)-2-Phenyl-2-(cyclopent-1-enyl)-1-nitroethene (3dm).** 84% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.41–7.38 (m, 3H), 7.16–7.13 (m, 2H), 7.08 (s, 1H), 5.88 (s, 1H), 2.59 (td,  $J = 7.6, 1.8$  Hz, 2H), 2.47 (td,  $J 7.1, 1.7$  Hz, 2H), 2.07 (p,  $J = 7.6$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  146.6, 146.3, 142.0, 135.2, 134.1, 128.2, 128.1, 127.6, 34.0, 31.9, 23.2; IR (film)  $\nu_{\max}$  3049, 2956, 2839, 1684, 1590, 1514, 1334, 698  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}_2$   $[\text{M}]$   $m/z$  216.10, found 216.09.

## 2.C.ii. Assignment of Stereochemistry via NOESY Spectroscopy

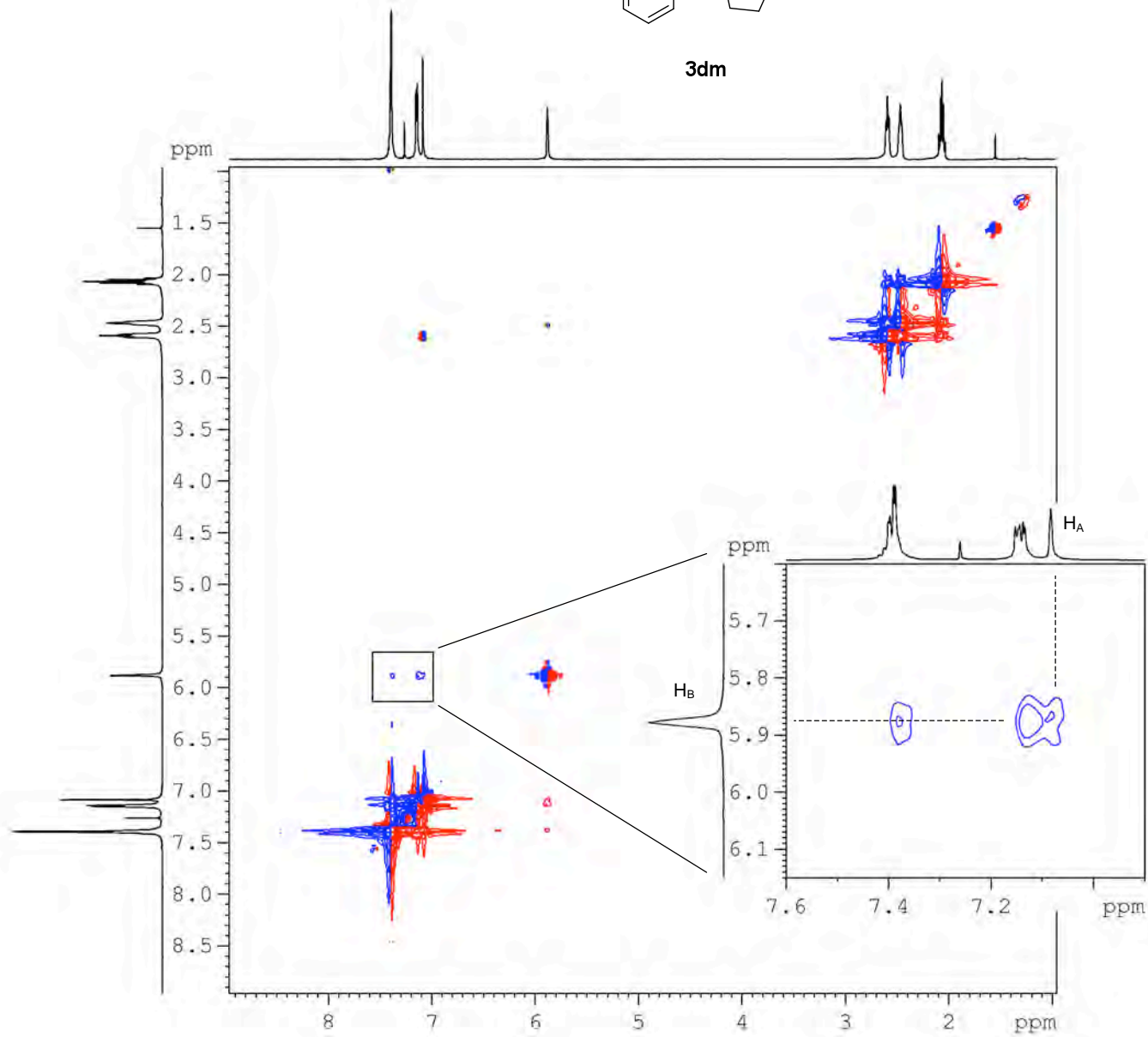
Nitrodienes and nitrostyrenes resulting from cross-coupling with acyclic vinyl thioethers **1c** and **1d** have the potential for stereoisomeric olefin configurations. In order to elucidate the major diastereomers of nitroorganics **3cc**, **3cj**, and **3dm**, NOESY spectroscopy was invoked.





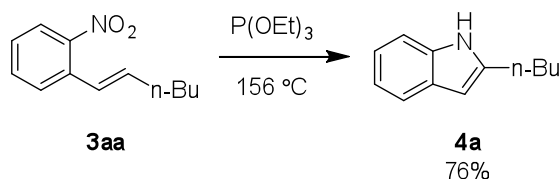


3dm



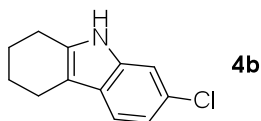
## 2.D. Cadogan Reductive Cyclization

### Representative Procedure



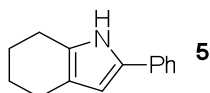
**2-Butylindole (4a).** The nitrostyrene **3aa** (20 mg, 0.097 mmol, 1.0 equiv) was added to a dry, argon-replenished reaction vessel equipped with a Teflon stirrer bar and condenser. Distilled triethyl phosphite (3 mL) was added and then the reaction vessel was submerged in a sand bath at ca.  $170\text{ }^\circ\text{C}$  to initiate a mild reflux. The reaction's progress was monitored using TLC (eluent: hexanes/EtOAc, 4:1; visualization: anisaldehyde stain; product  $R_f = \text{ca. } 0.5$ ); the reaction time (from 1 h to 24 h) was very substrate-dependant. Once complete, the volatiles were evaporated with careful application of a high vacuum (ca. 1 mmHg), rapid stirring, and a  $-78\text{ }^\circ\text{C}$  trap to capture remaining triethyl phosphite. The crude residue was loaded onto a silica gel column and purified through flash chromatography (eluent: 5% EtOAc/hexanes) to yield a light-brown solid (12.8 mg, 76%). Spectroscopic characteristics were identical to those reported previously.<sup>14</sup>

### 2.D.i. Physical and Spectroscopic data for *N*-Heteroaromatics **4** and **5**



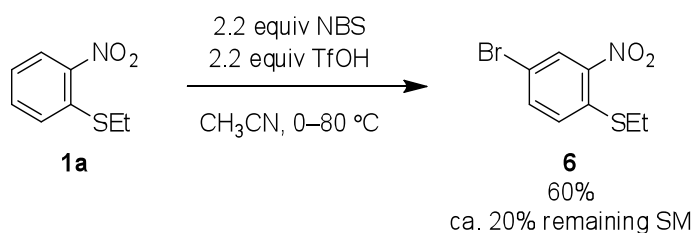
<sup>14</sup> Hegedus, L. S.; Winton, P. M.; Varaprath, S. *J. Org. Chem.* **1981**, *46*, 2215.

**7-Chloro-1,2,3,4-tetrahydrocarbazole (4b)**. 55% yield. Spectroscopic characteristics were identical to those reported previously.<sup>15</sup>



**2-Phenyl-4,5,6,7-tetrahydroindole (5)**. 74% yield. Spectroscopic characteristics were identical to those reported previously.<sup>16</sup>

## 2.E. Demonstration of Orthogonality with Suzuki–Miyaura Coupling

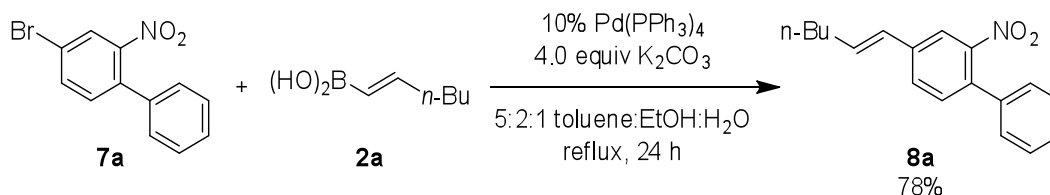


**5-Bromo-2-ethylthio-1-nitrobenzene (6)**. *N*-Bromosuccinimide (534 mg, 3.0 mmol, 2.2 equiv), acetonitrile (distilled, 25 mL), and 1-ethylthio-2-nitrobenzene (250 mg, 1.36 mmol, 1 equiv) were added sequentially to a dry, argon-replenished, round-bottom flask equipped with a condenser. The mixture was cooled to 0 °C and then triflic acid (265 μL, 3.0 mmol, 2.2 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h, then warmed to 22 °C over 1 h, before being moved to an oil bath and gradually heated to reflux over 4 h. The reaction's progress was monitored by TLC (hexanes: EtOAc, 4:1), noting the disappearance of the starting material and transient sulfoxide; the disappearance of the sulfoxide was complete after heating

<sup>15</sup> For <sup>1</sup>H NMR spectroscopic data: Chen, J.; Hu, Y. *Synth. Commun.* **2006**, *36*, 1485. For <sup>13</sup>C NMR spectroscopic data: Simoneau, C. A.; Strohl, A. M.; Ganem, B. *Tetrahedron Lett.* **2007**, *48*, 1809.

<sup>16</sup> Hiroya, K.; Matsumoto, S.; Ashikawa, M.; Ogiwara, K.; Sakamoto, T. *Org. Lett.* **2006**, *8*, 5349.

under reflux for 18 h, although a slight amount of the starting material remained. The reaction mixture was poured into a separatory funnel containing 20% saturated NaHCO<sub>3</sub> (25 mL) and EtOAc (40 mL) and the layers separated. The organic phase was washed with water (25 mL) and brine (25 mL); the combined organic phases were dried (MgSO<sub>4</sub>) and filtered and the volatiles evaporated in vacuo. The crude residue was loaded onto a silica gel column and purified through flash chromatography (5% EtOAc in hexanes). Recrystallization (hexanes) of the isolated product afforded a bright yellow solid (214 mg, 60%). M.p. 115–116 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.35 (d, *J* = 2.2 Hz, 1H), 7.65 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 2.98 (q, *J* = 7.4 Hz, 2H), 1.41 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 146.2, 137.2, 136.2, 128.8, 127.7, 117.0, 26.3, 12.7; IR (film) ν<sub>max</sub> 3113, 2961, 1538, 1509, 1450, 1339, 814, 750 cm<sup>-1</sup>; MS (GCMS) calcd for C<sub>8</sub>H<sub>8</sub>NO<sub>2</sub>BrS [M] *m/z* 260.9, found 260.9.

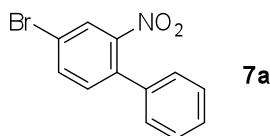


**(E)-4-(Hex-1-enyl)-2-nitrobiphenyl (8a).** Prepared through adaptation of an analogous literature procedure for related compounds.<sup>17</sup> A dry, argon-replenished reaction vessel equipped with a reflux condenser was charged with K<sub>2</sub>CO<sub>3</sub> (111 mg, 0.80 mmol, 4.0 equiv), (E)-hexenylboronic acid **2a** (38.4 mg, 0.30 mmol, 1.5 equiv), and palladium tetrakis(triphenylphosphine) (23.1 mg, 0.020 mmol, 0.10 equiv). The solid mixture was vacuum-replenished with argon and then a solution of the aryl thioether **7a** (55.6 mg, 0.20 mmol, 1.0 equiv) in toluene (3.75 mL), ethanol (1.5 mL), and water (0.75 mL) was added. The solution was

<sup>17</sup> Shen, M.; Leslie, B. E.; Driver, T. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5056.

stirred under reflux under a positive pressure of argon. The reaction's progress was monitored by TLC (hexanes:EtOAc, 4:1; product  $R_f = 0.65$ ), with complete consumption of the starting aryl bromide within 24 h. The reaction was quenched through the addition of EtOAc (20 mL) and saturated ammonium chloride (15 mL); the layers were separated and the organic phase washed successively with water (15 mL) and brine ( $2 \times 15$  mL). The combined aqueous phases were back-extracted with EtOAc (10 mL); the combined organic phases were dried ( $\text{MgSO}_4$ ). After evaporation of the solvent under reduced pressure, the crude residue was loaded onto a silica gel column and purified through flash chromatography (hexanes/benzene/EtOAc, gradient from 89:10:1 to 84:10:6) to yield a light-yellow oil (43.7 mg, 78%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.80 (d,  $J = 1.8$  Hz, 1H), 7.54 (dd,  $J = 8.0, 1.8$  Hz, 1H), 7.44–7.38 (m, 3H), 7.36 (d,  $J = 8.0$  Hz, 1H), 7.32–7.30 (m, 2H), 6.45–6.34 (m, 2H), 2.27 (q,  $J = 6.9$  Hz, 2H), 1.49 (p,  $J = 7.4$  Hz, 2H), 1.40 (sextet,  $J = 7.4$  Hz, 2H), 0.95 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  149.5, 138.6, 137.3, 134.7, 134.1, 132.0, 129.3, 128.6, 128.1, 127.9, 127.3, 121.1, 32.7, 31.2, 22.2, 13.9; IR (film)  $\nu_{\text{max}}$  3040, 2933, 2864, 1528, 1352, 964, 772, 694  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{18}\text{H}_{19}\text{NO}_2$  [M]  $m/z$  281.1, found 281.2.

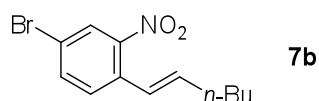
### 2.E.i. Physical and Spectroscopic Data for Compounds 7–9



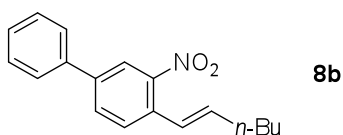
**4-Bromo-2-nitrobiphenyl (7a).** 83% yield, using the general procedure described in Section 2.B.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.00 (d,  $J = 2.0$  Hz, 1H), 7.75 (dd,  $J = 8.2, 2.0$  Hz, 1H), 7.44–7.42 (m, 3H), 7.33 (d,  $J = 8.2$  Hz, 1H), 7.30–7.28 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$



149.5, 136.3, 135.3, 135.2, 133.2, 128.8, 128.6, 127.7, 127.0, 121.3; IR (film)  $\nu_{\max}$  3066, 2938, 1596, 1526, 1345, 1007, 698, 663  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{12}\text{H}_8\text{NO}_2\text{Br}$  [M]  $m/z$  277.0, found 277.0.

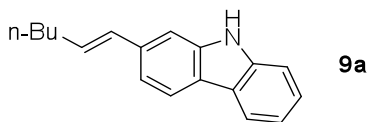


**(E)-5-Bromo-2-(hex-1-enyl)-1-nitrobenzene (7b).** 62% yield, using the general procedure described in Section 2.B.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.01 (d,  $J = 2.1$  Hz, 1H), 7.63 (dd,  $J = 8.5, 2.0$  Hz, 1H), 7.46 (d,  $J = 8.5$  Hz, 1H), 6.76 (d,  $J = 15.7$  Hz, 1H), 6.25 (dt,  $J = 15.6, 7.0$  Hz, 1H), 2.26 (qd,  $J = 7.2, 1.3$  Hz, 2H), 1.47 (p,  $J = 7.4$  Hz, 2H), 1.38 (sextet,  $J = 7.4$  Hz, 2H), 0.93 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  147.7, 137.7, 135.7, 132.2, 129.6, 127.1, 123.8, 120.1, 32.8, 30.9, 22.1, 13.8; IR (film)  $\nu_{\max}$  2961, 2926, 2862, 1526, 1339, 1124, 966, 663  $\text{cm}^{-1}$ ; MS (GCMS) calcd for  $\text{C}_{12}\text{H}_{14}\text{NO}_2\text{Br}$  [M]  $m/z$  283.0, found 283.0.

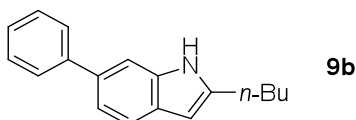


**(E)-4-(Hex-1-enyl)-3-nitrobiphenyl (8b).** 99% yield, using the general Suzuki–Miyaura procedure described in Section 2.D.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.10 (d,  $J = 1.9$  Hz, 1H), 7.75 (dd,  $J = 8.2, 1.8$  Hz, 1H), 7.66 (d,  $J = 8.2$  Hz, 1H), 7.62–7.59 (m, 2H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.40 (tt,  $J = 3.6, 1.5$  Hz, 1H), 6.86 (d,  $J = 15.7$  Hz, 1H), 6.30 (dt,  $J = 15.6, 6.9$  Hz, 1H), 2.30 (qd,  $J = 7.2, 1.4$  Hz, 2H), 1.51 (p,  $J = 7.4$  Hz, 2H), 1.41 (sextet,  $J = 7.3$  Hz, 2H), 0.95 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  148.1, 140.6, 138.4, 137.0, 131.9, 131.0, 129.1, 128.7, 128.3,

126.9, 124.5, 122.6, 32.9, 31.1, 22.2, 13.9; IR (film)  $\nu_{\max}$  2956, 2915, 2856, 1649, 1526, 1357, 762, 692  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}_2$   $[\text{M} + \text{H}]^+$   $m/z$  282.15, found 282.14.



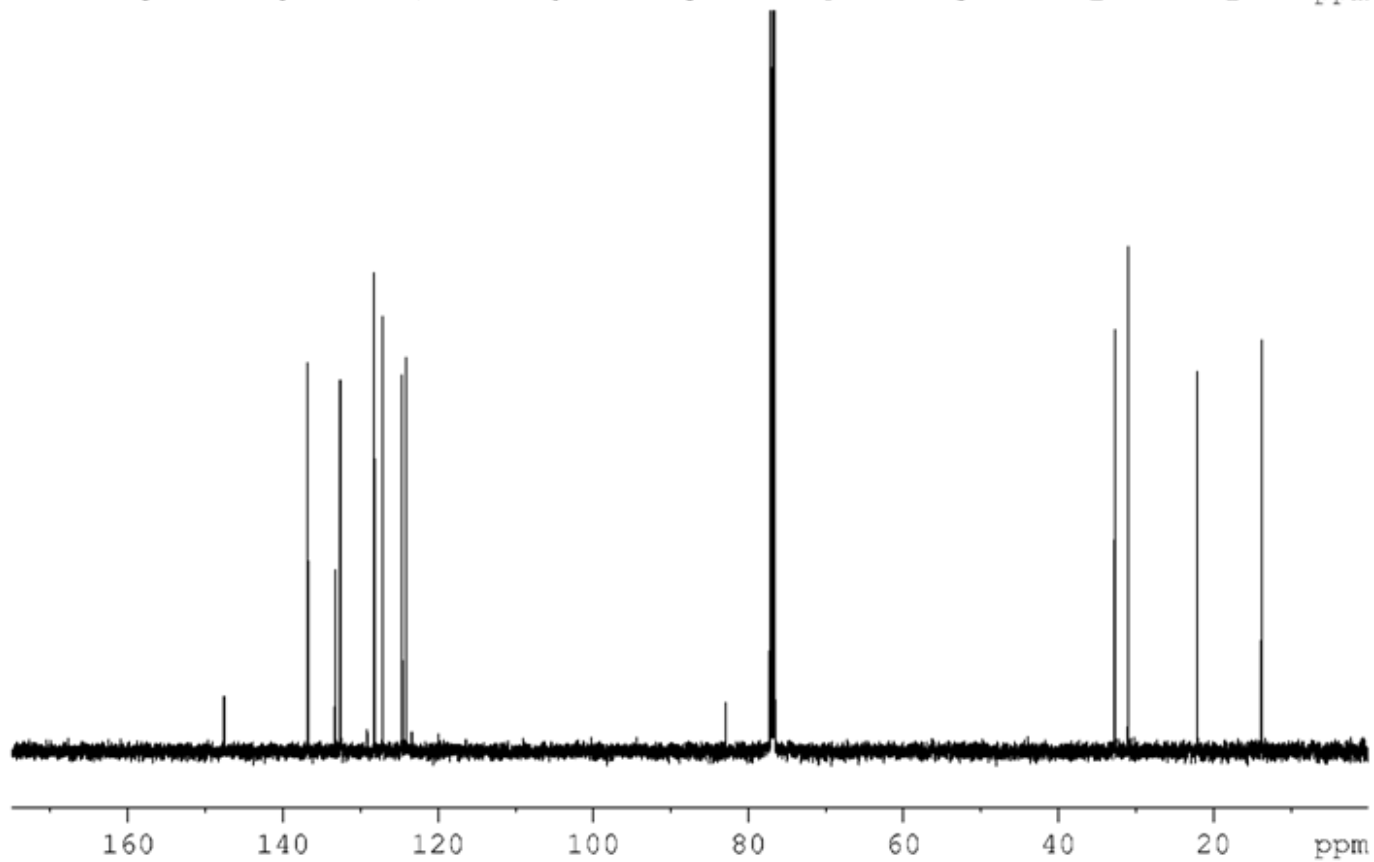
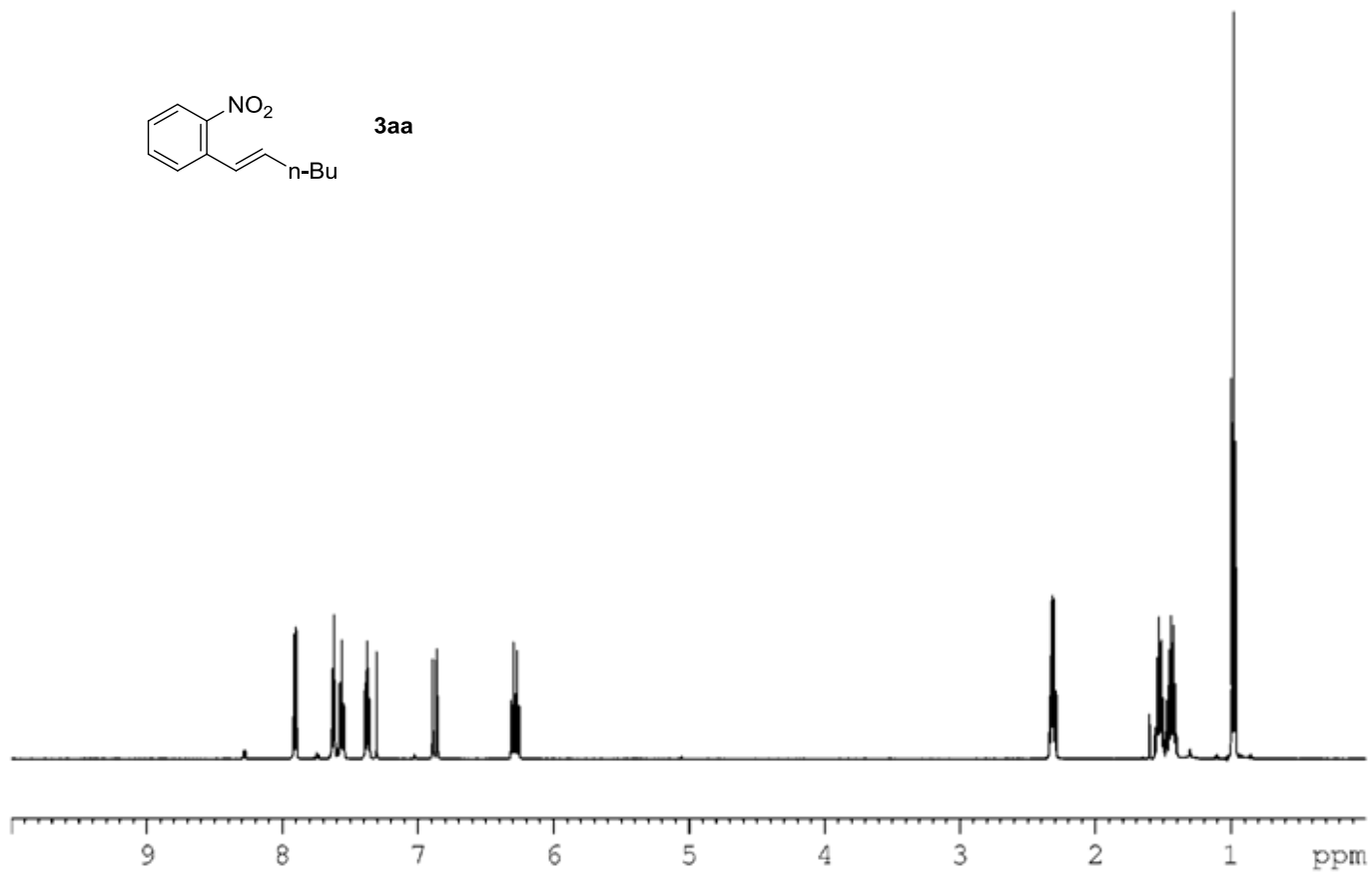
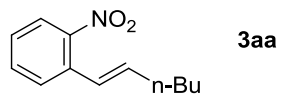
**(E)-2-(Hex-1-enyl)-carbazole (9a).** 75% yield, using the general procedure described in Section 2.C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.03 (d,  $J = 7.8$  Hz, 1H), 7.98 (br s, 1H), 7.97 (d,  $J = 8.0$  Hz, 1H), 7.42–7.36 (m, 3H), 7.28 (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.22 (ddd,  $J = 7.9, 6.3, 1.6$  Hz, 1H), 6.53 (d,  $J = 15.8$  Hz, 1H), 6.32 (dt,  $J = 15.7, 7.0$  Hz, 1H), 2.25 (qd,  $J = 7.1, 1.3$  Hz, 2H), 1.50 (p,  $J = 7.4$  Hz, 2H), 1.41 (sextet,  $J = 7.3$  Hz, 2H), 0.95 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  140.0, 139.8, 136.1, 130.8, 130.4, 125.5, 123.4, 122.4, 120.3, 120.1, 119.5, 118.0, 110.5, 107.8, 32.8, 31.6, 22.3, 14.0; IR (film)  $\nu_{\max}$  3399, 2956, 2909, 1444, 1339, 1322, 960, 727  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{18}\text{H}_{20}\text{N}$   $[\text{M} + \text{H}]^+$   $m/z$  250.161, found 250.159.

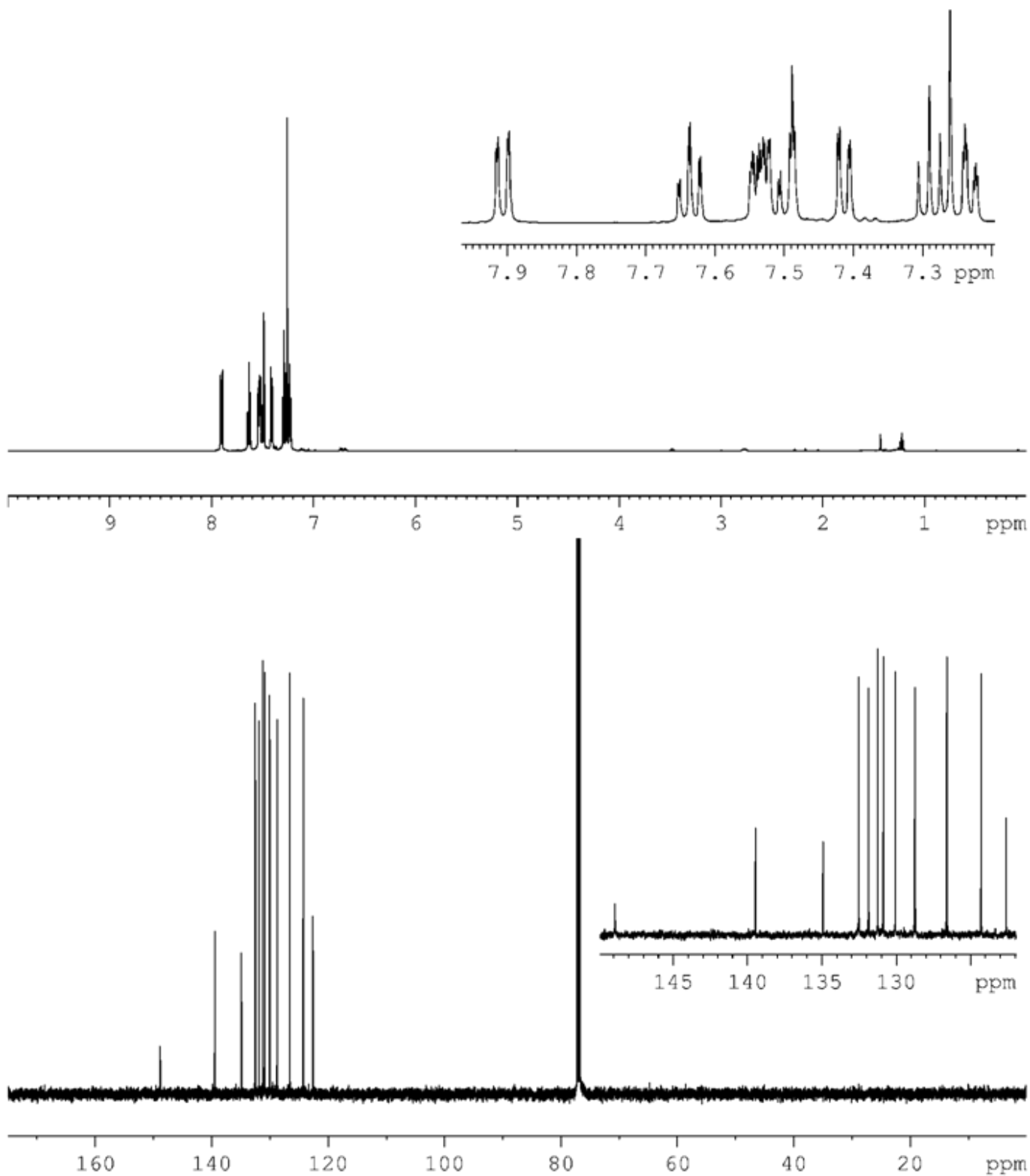
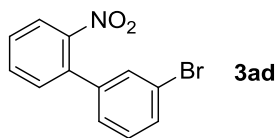


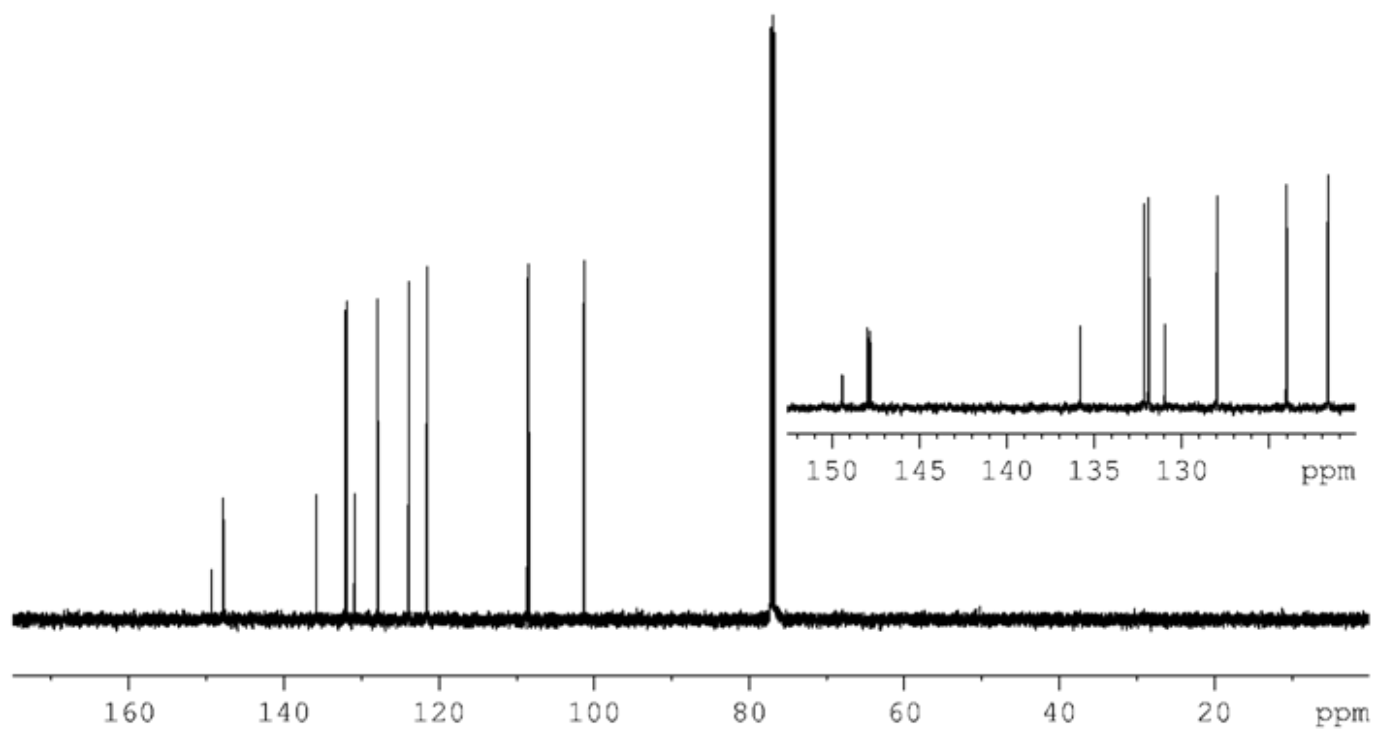
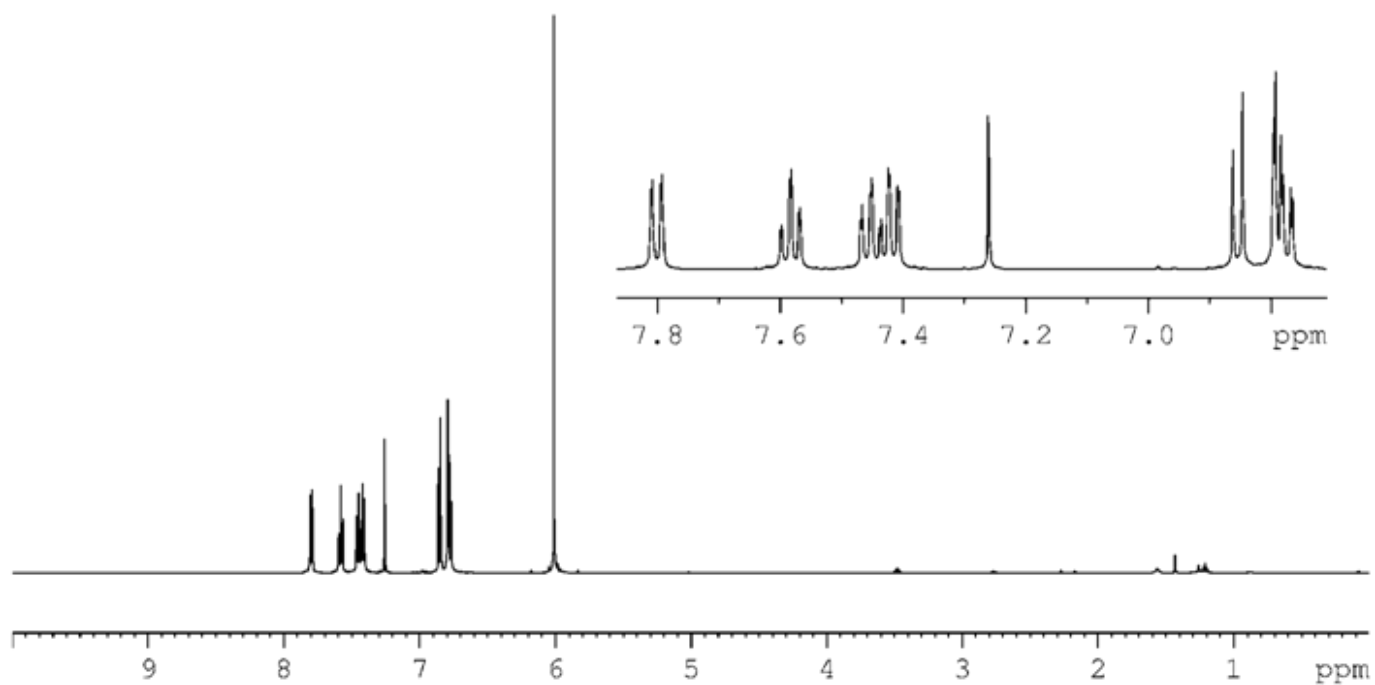
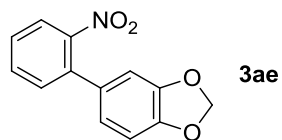
**2-Butyl-6-phenyl-indole (9b).** 72% yield, using the general procedure described in Section 2.C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.92 (br s, 1H), 7.64 (dd,  $J = 8.2, 1.2$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 1H), 7.51 (s, 1H), 7.43 (t,  $J = 7.8$  Hz, 2H), 7.33 (dd,  $J = 8.1, 1.6$  Hz, 1H), 7.30 (t,  $J = 6.8$  Hz, 1H), 6.26 (br s, 1H), 2.78 (t,  $J = 7.6$  Hz, 2H), 1.73 (p,  $J = 7.6$  Hz, 2H), 1.44 (sextet,  $J = 7.5$  Hz, 2H), 0.96 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  142.4, 140.7, 136.3, 134.4, 128.5, 128.1, 127.2, 126.3, 119.8, 119.4, 108.7, 99.3, 31.2, 27.9, 22.3, 13.8; IR (film)  $\nu_{\max}$  3393, 2932,

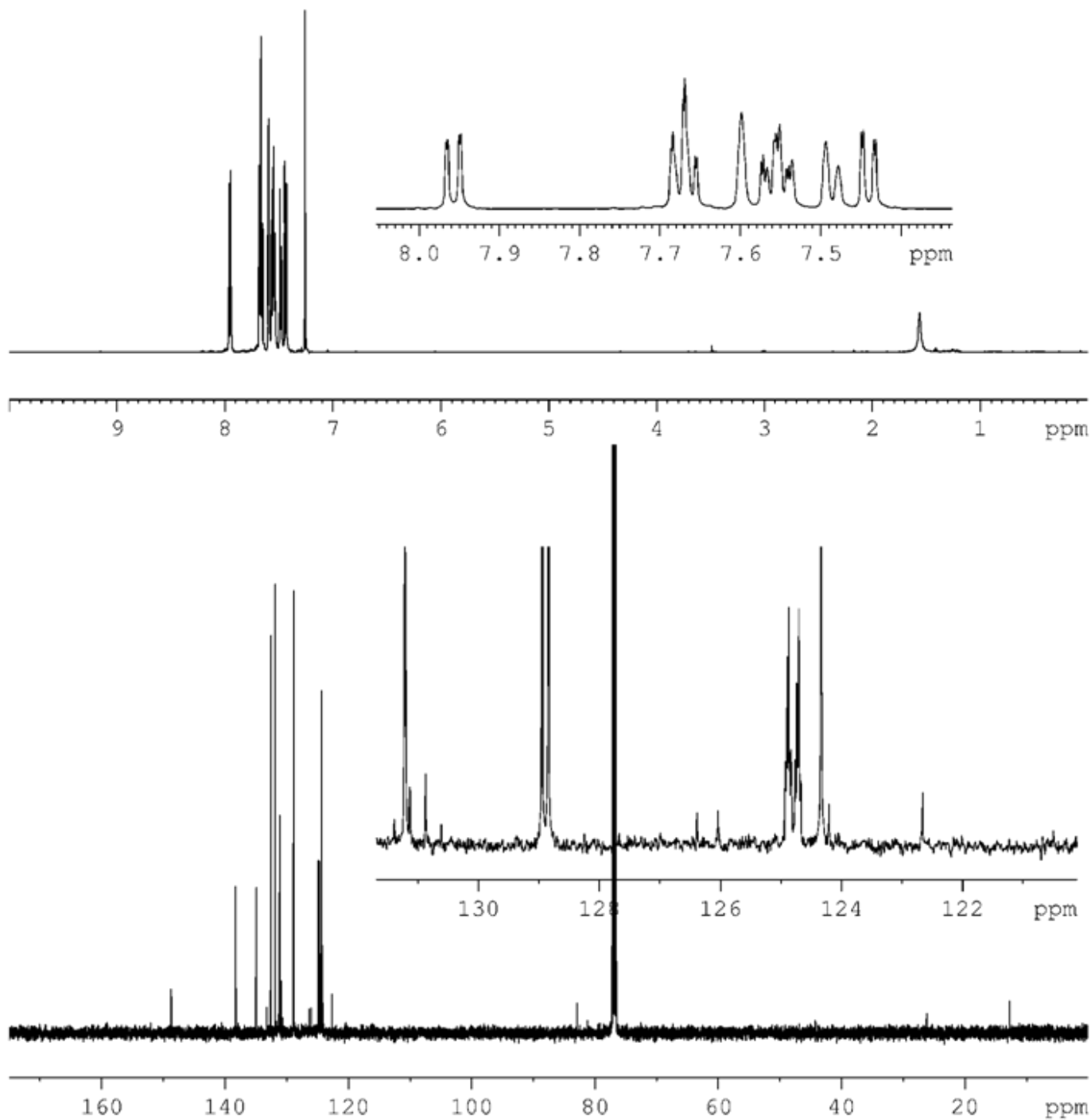
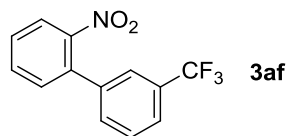
1649, 1549, 1503, 1462, 820, 744  $\text{cm}^{-1}$ ; MS (MALDI-TOF) calcd for  $\text{C}_{18}\text{H}_{20}\text{N}$   $[\text{M} + \text{H}]^+$   $m/z$   
250.16, found 250.15.

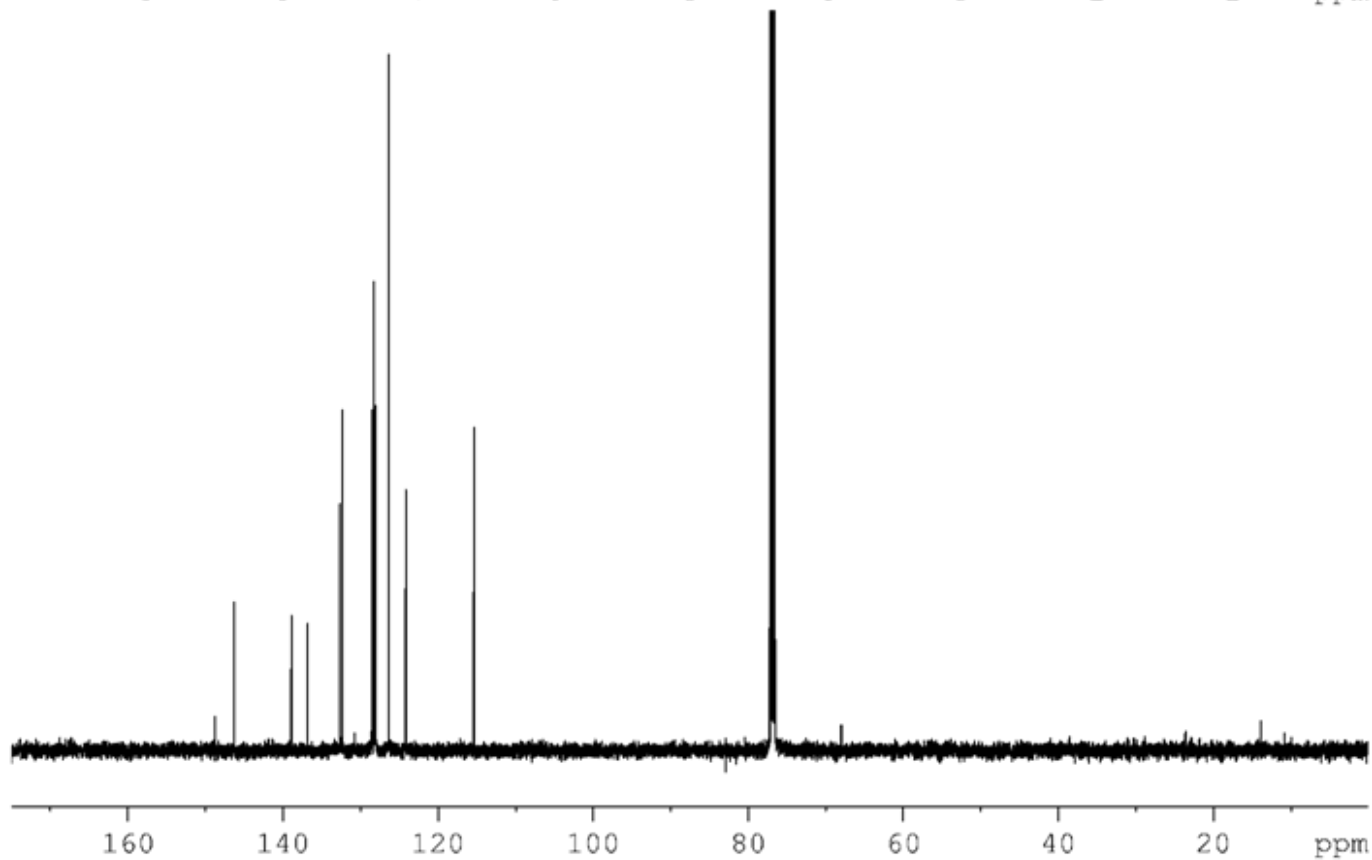
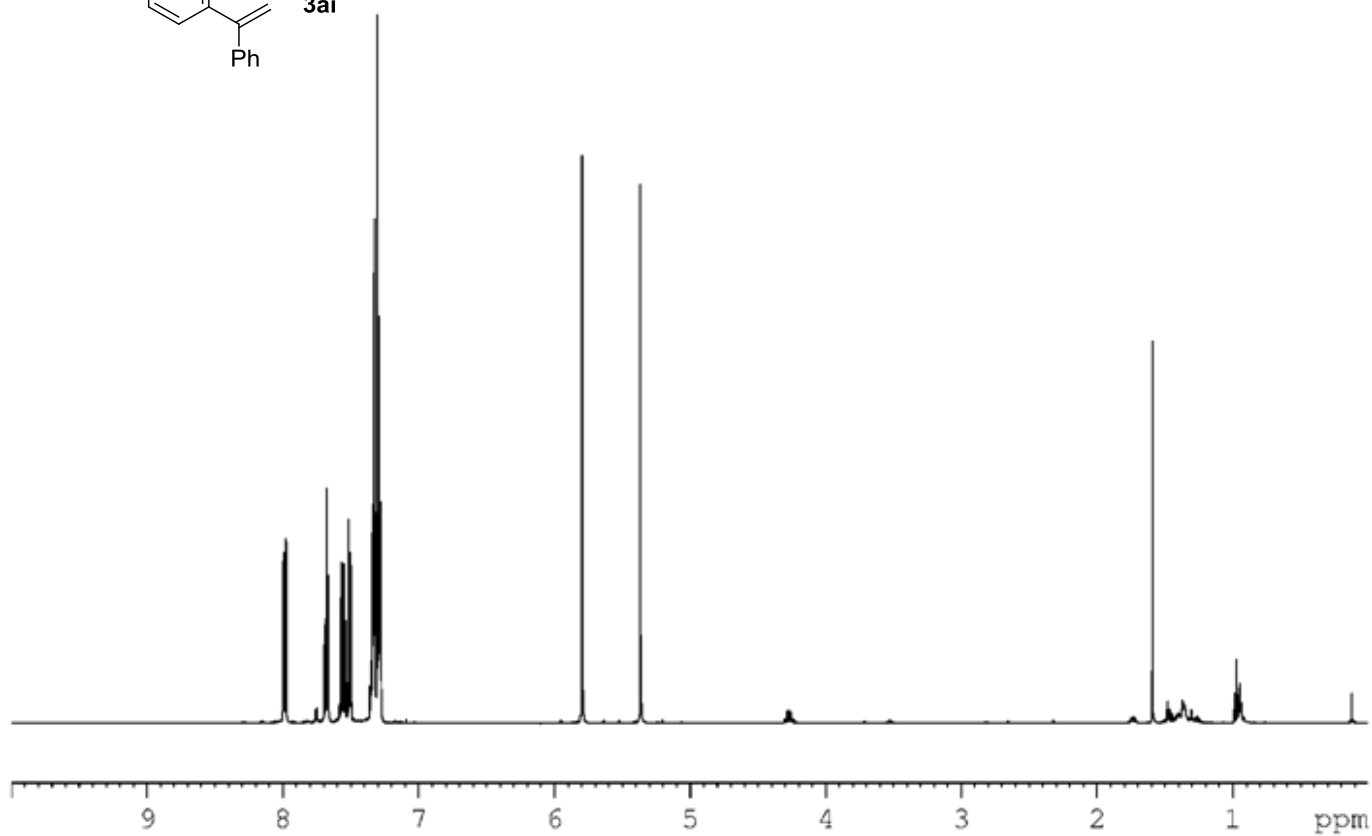
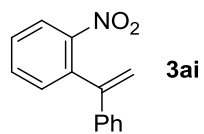
### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of New Compounds



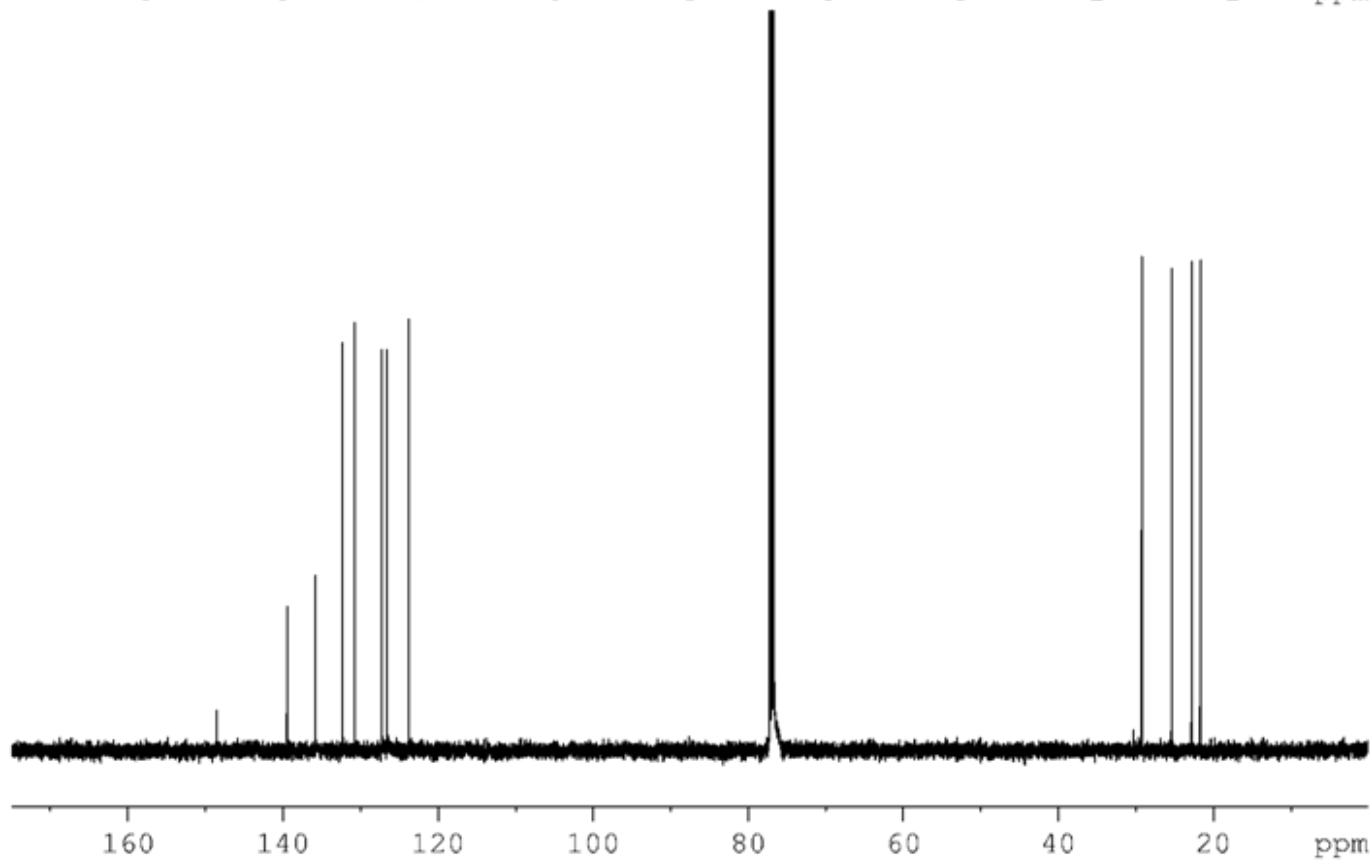
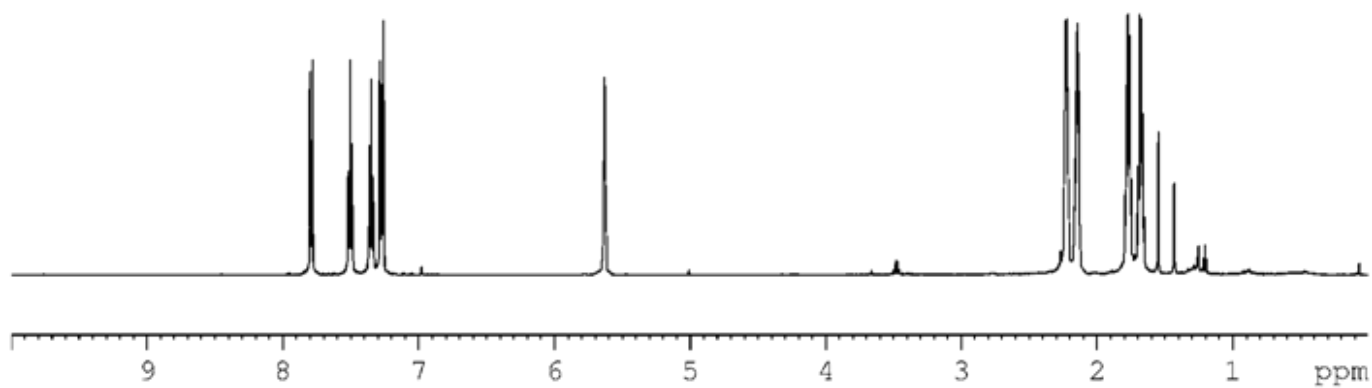
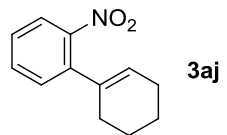


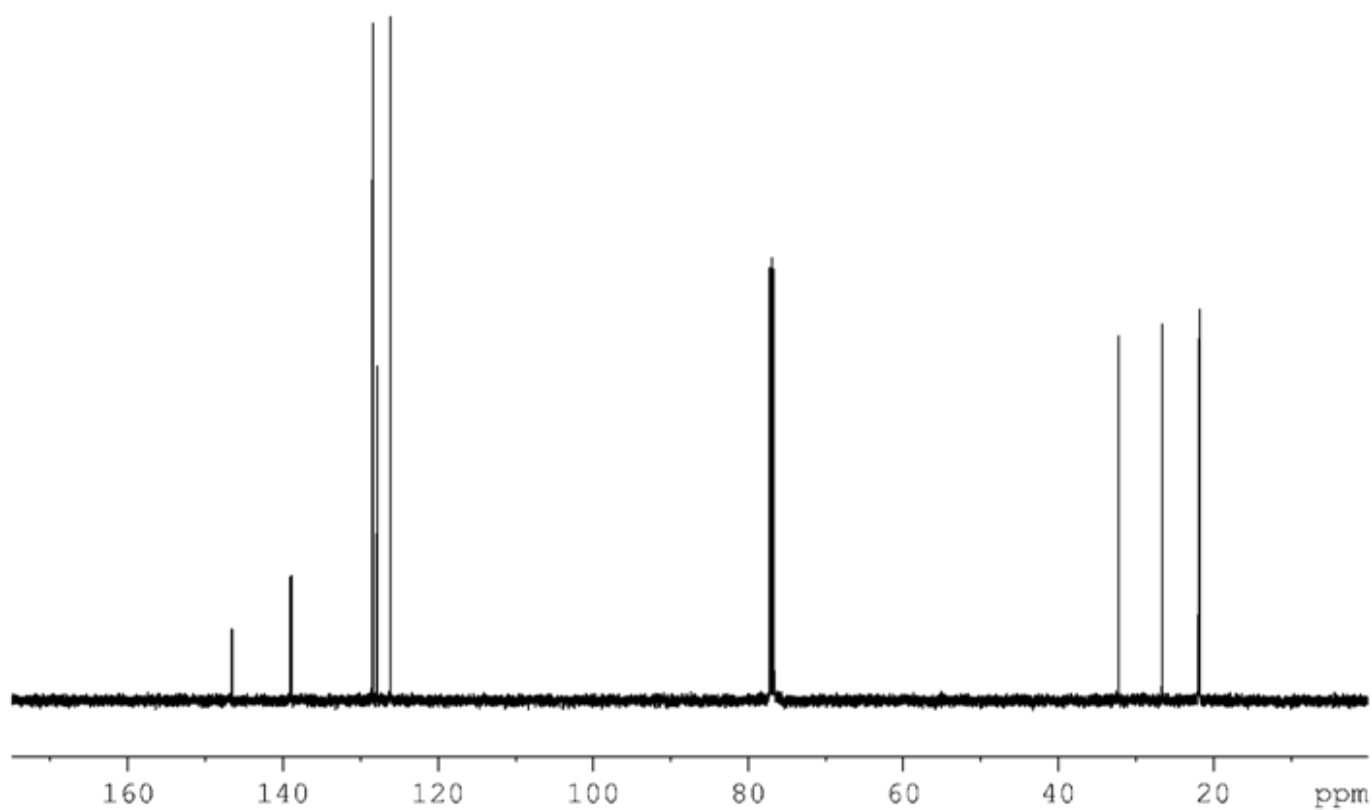
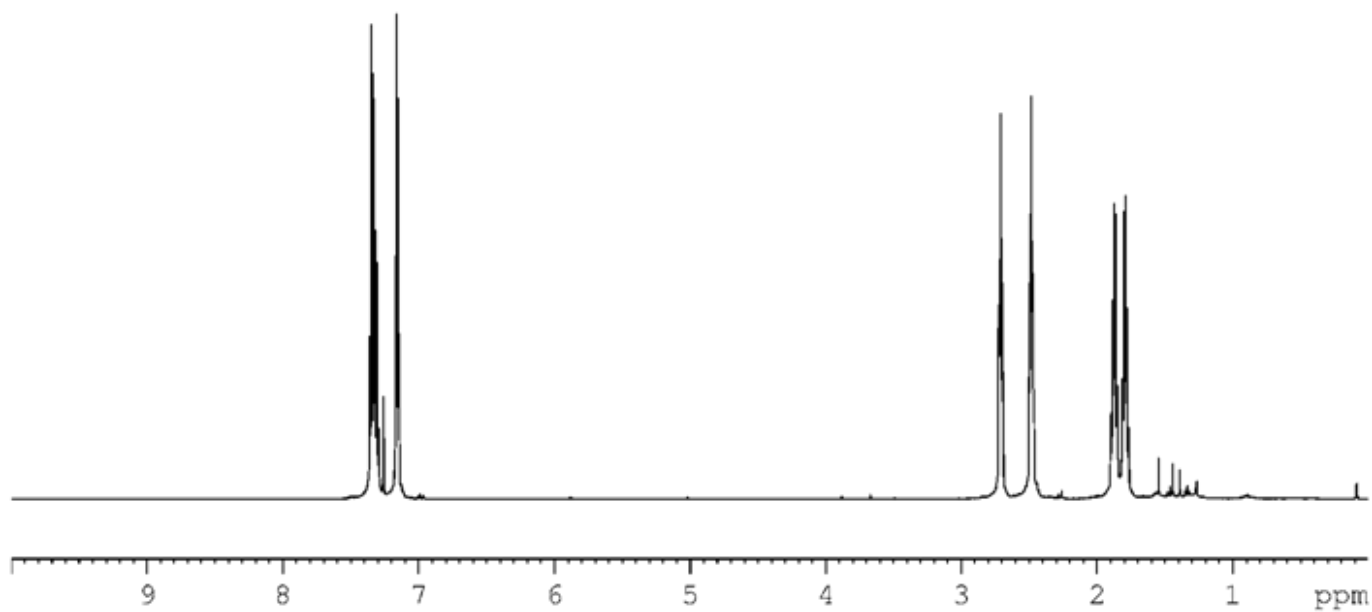
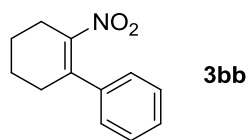


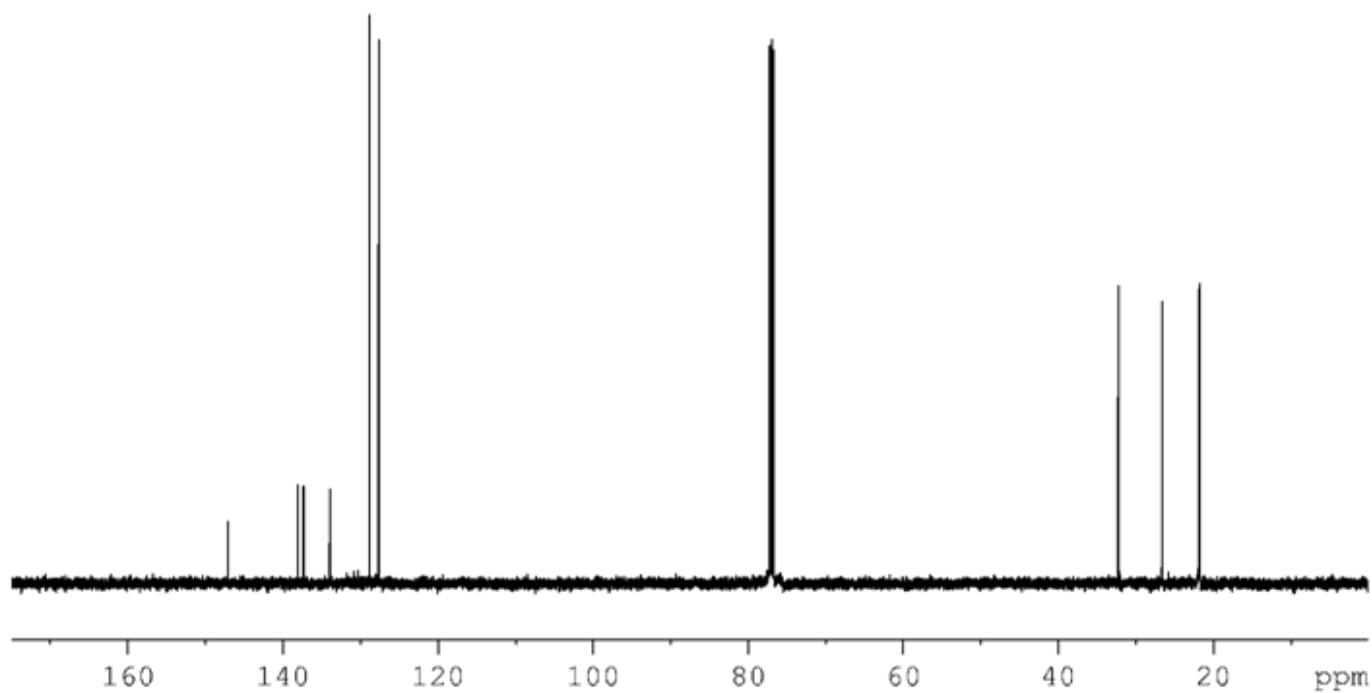
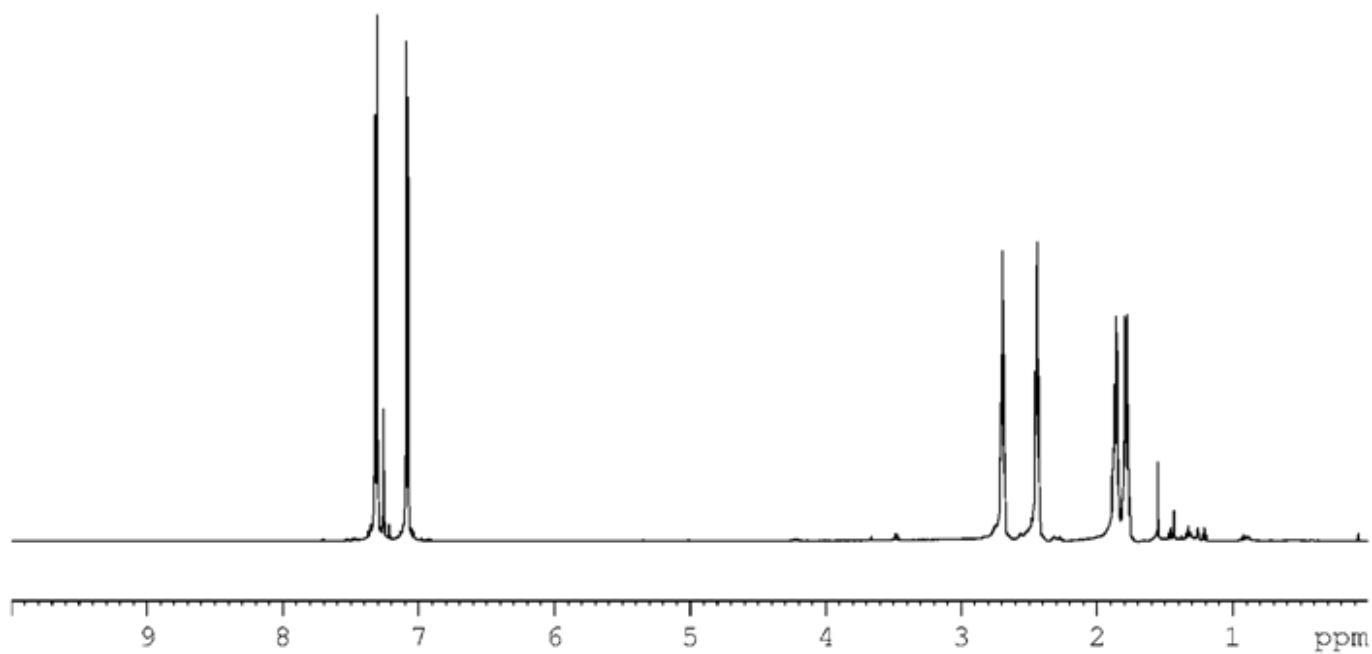
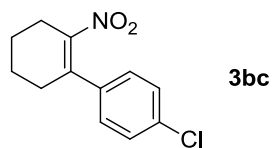


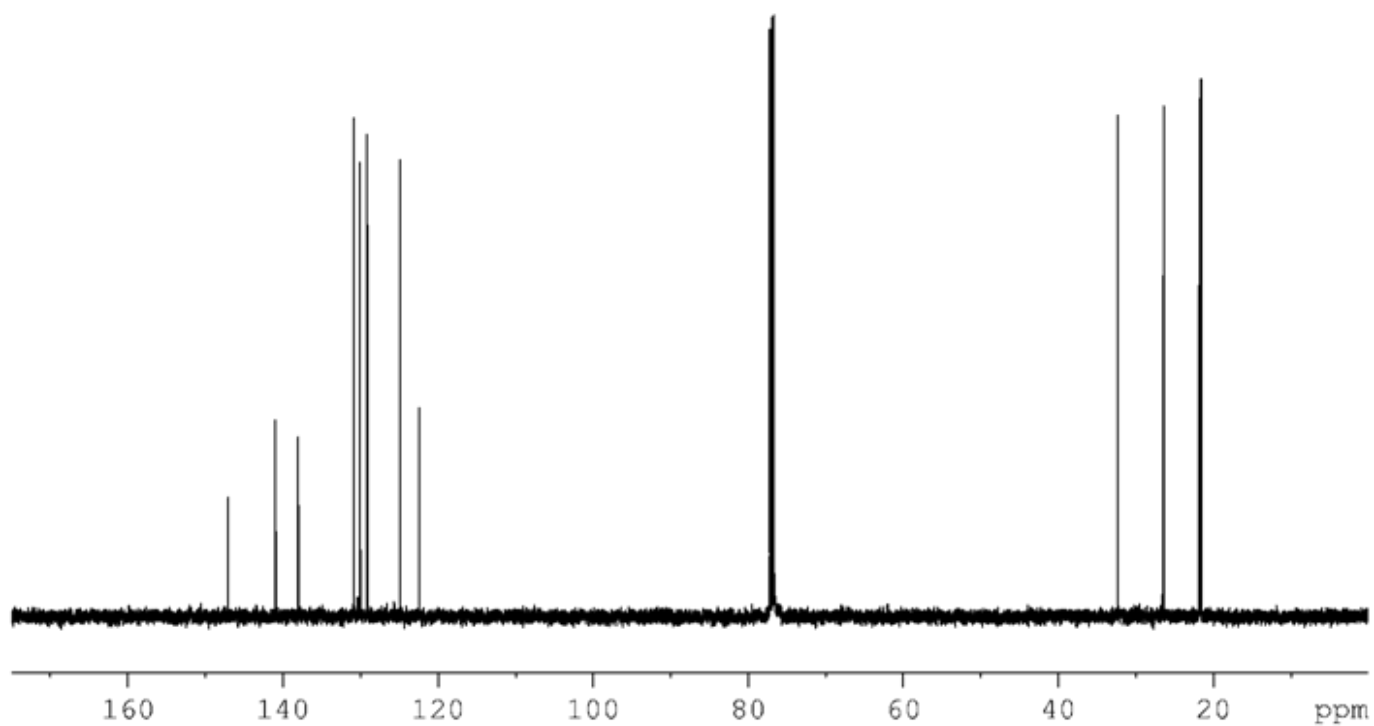
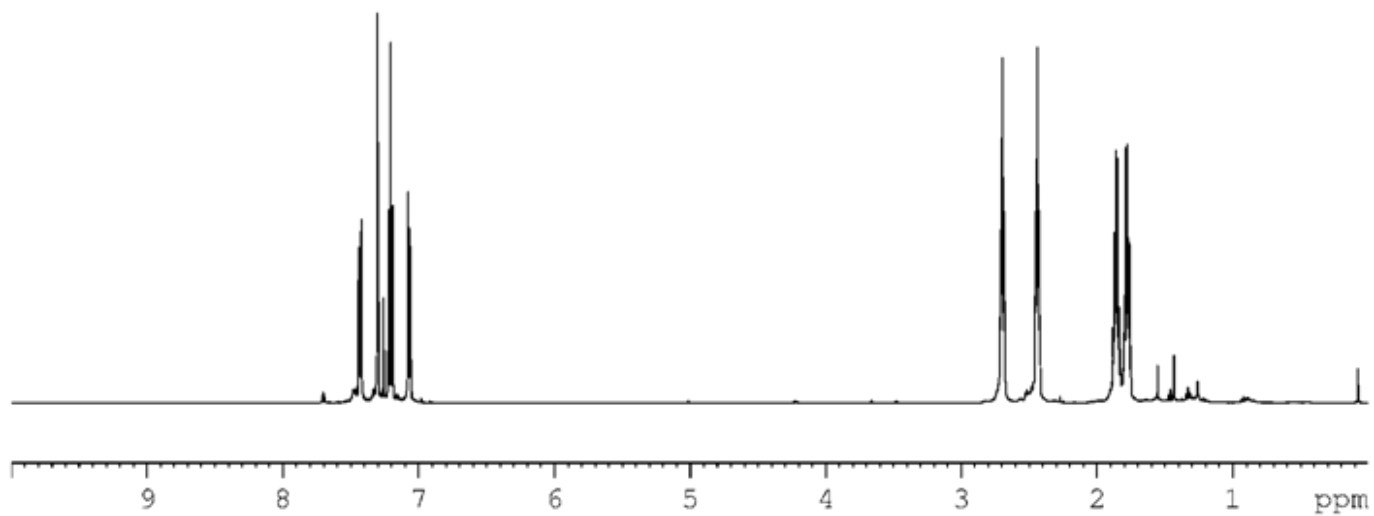
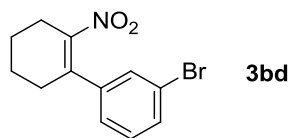


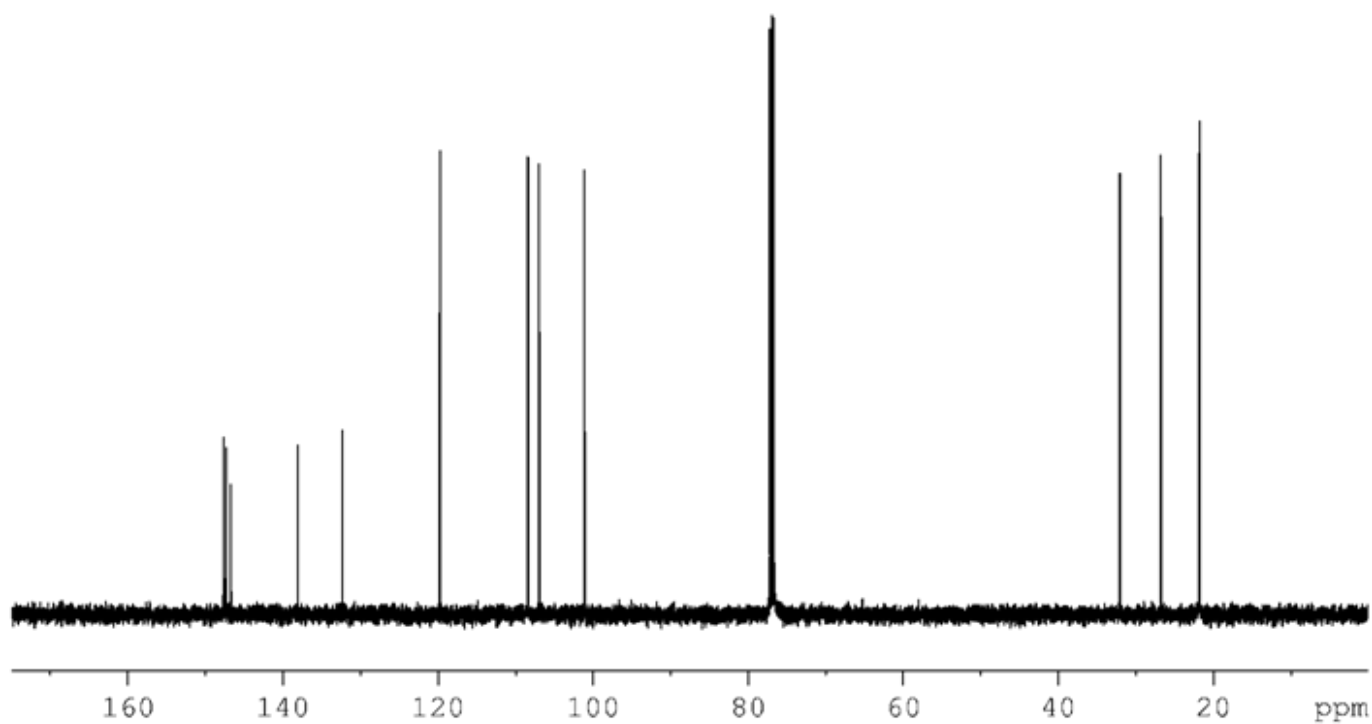
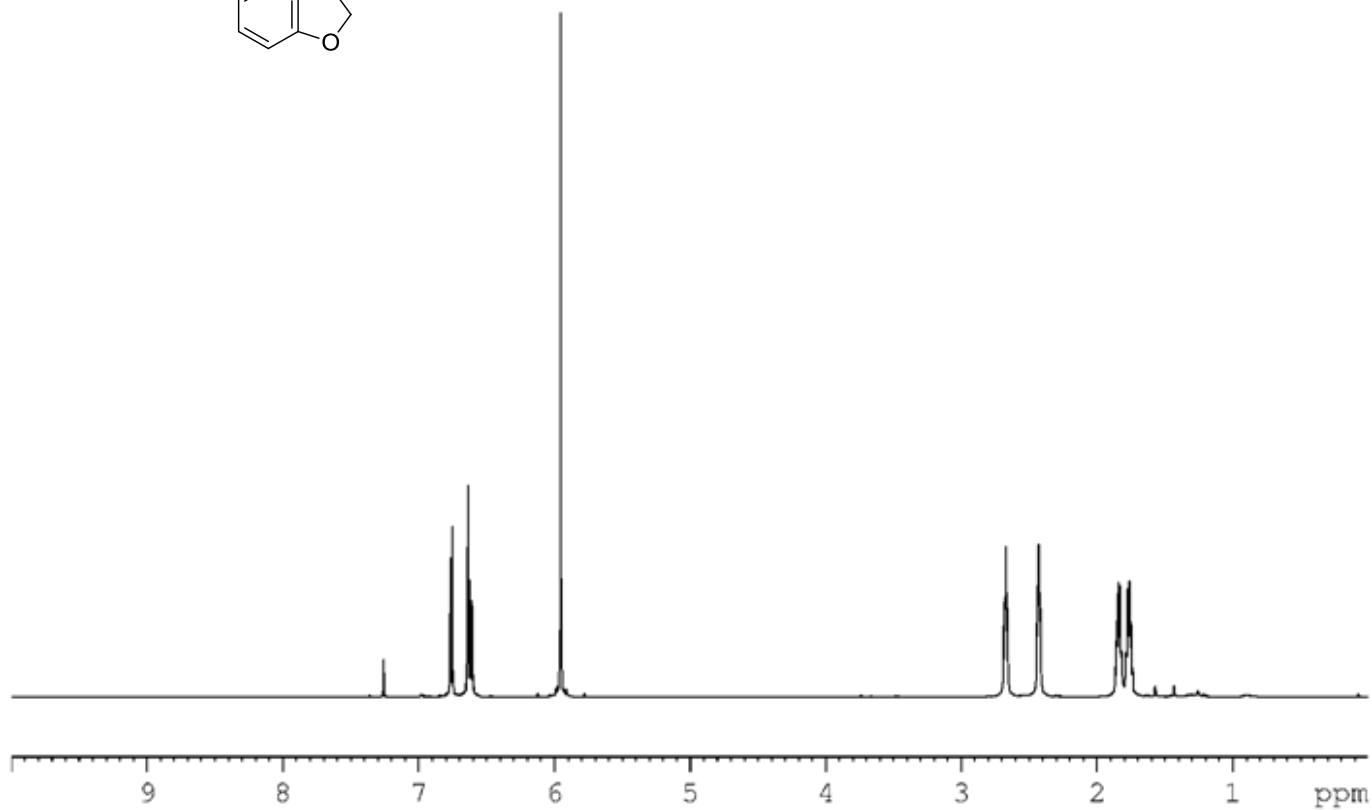
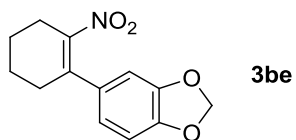


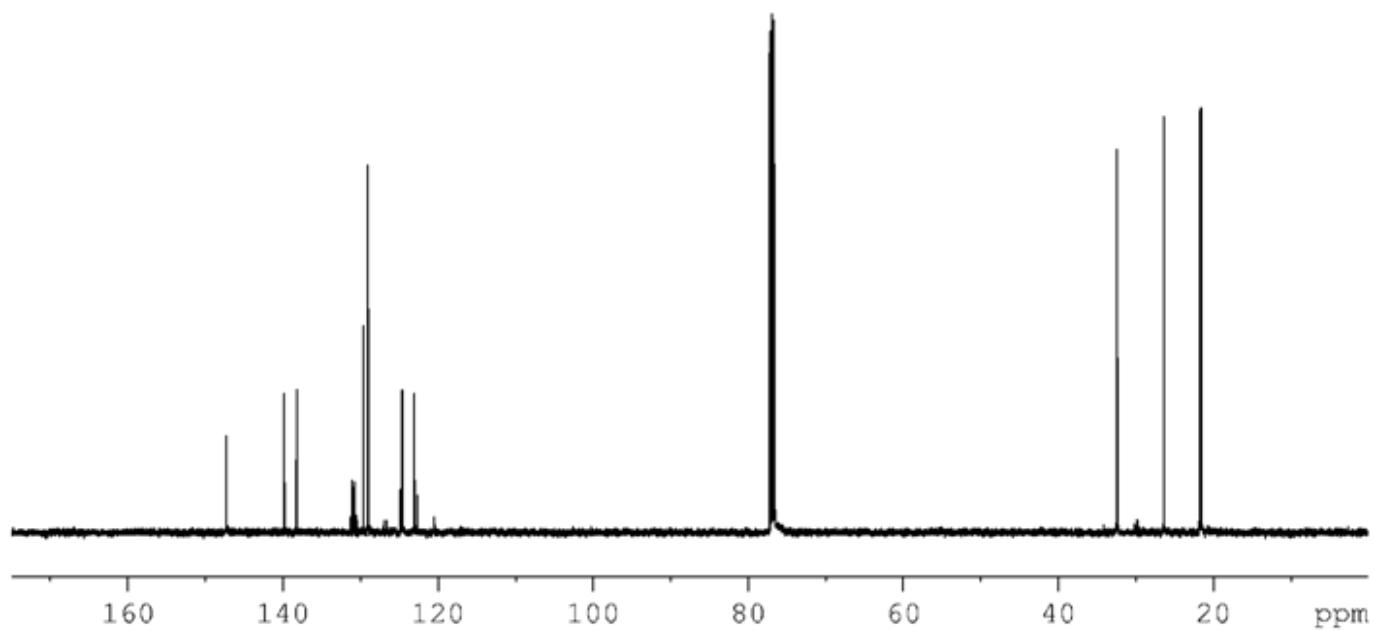
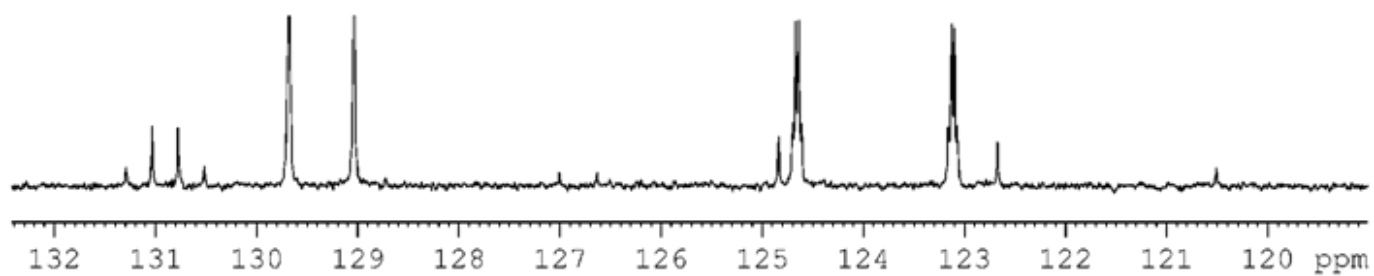
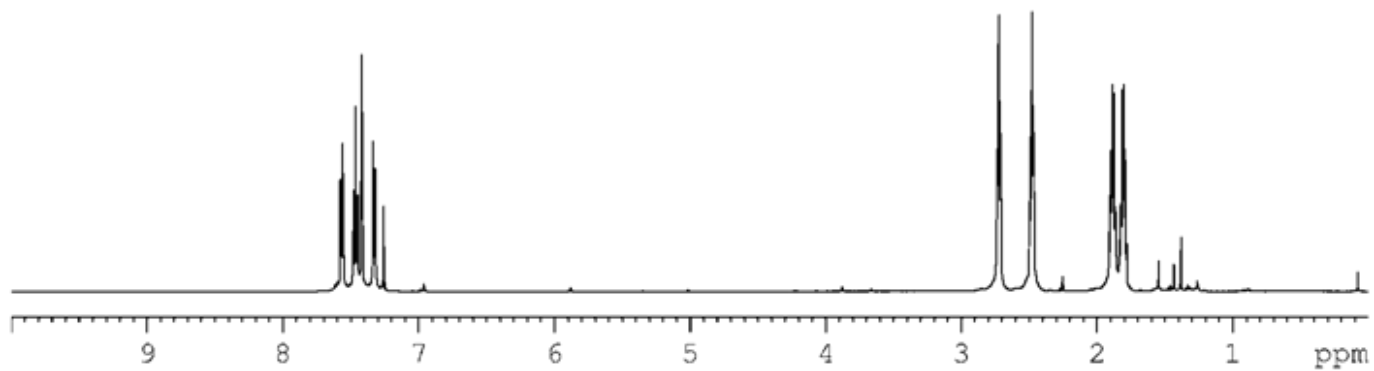
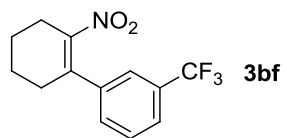


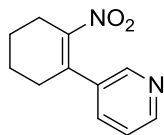




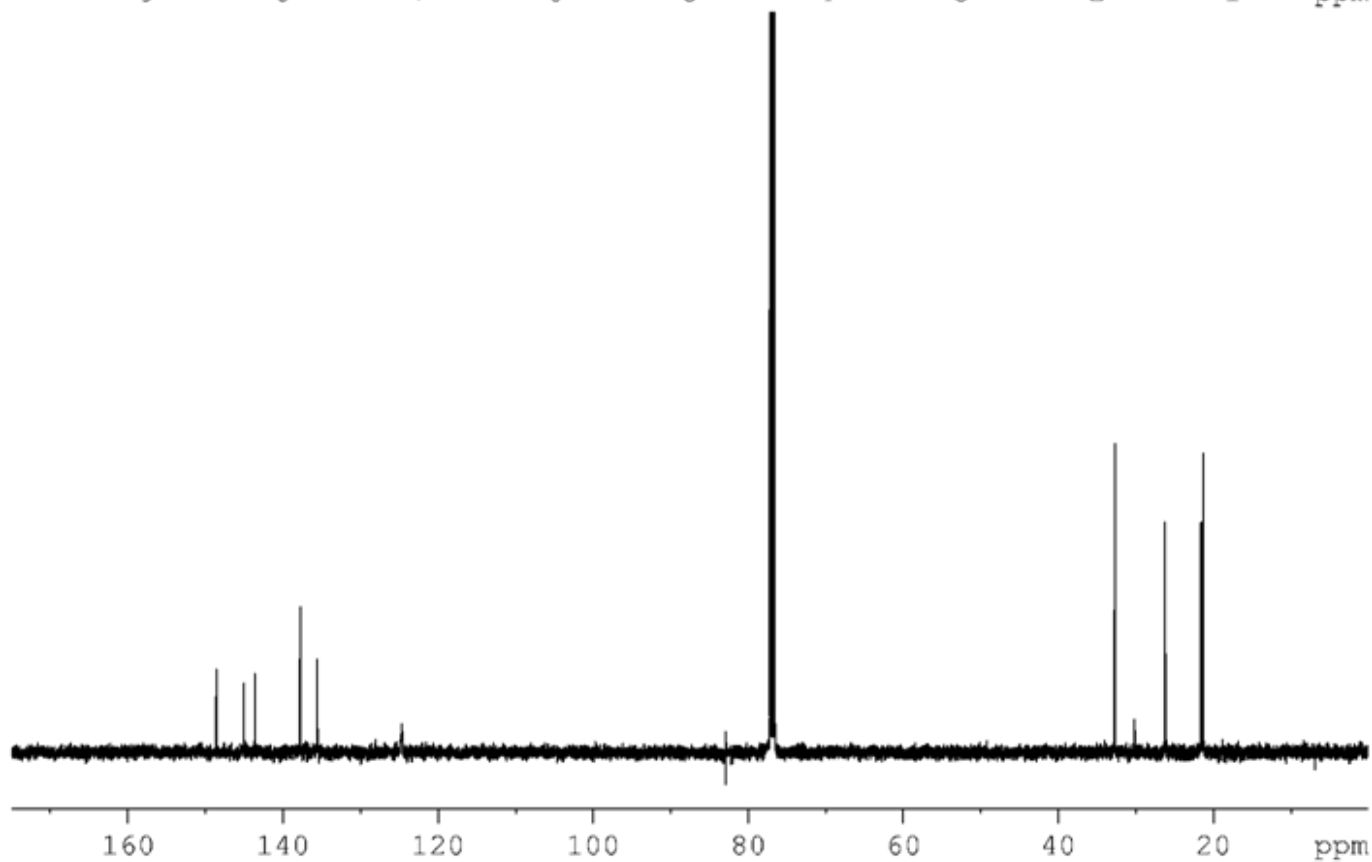
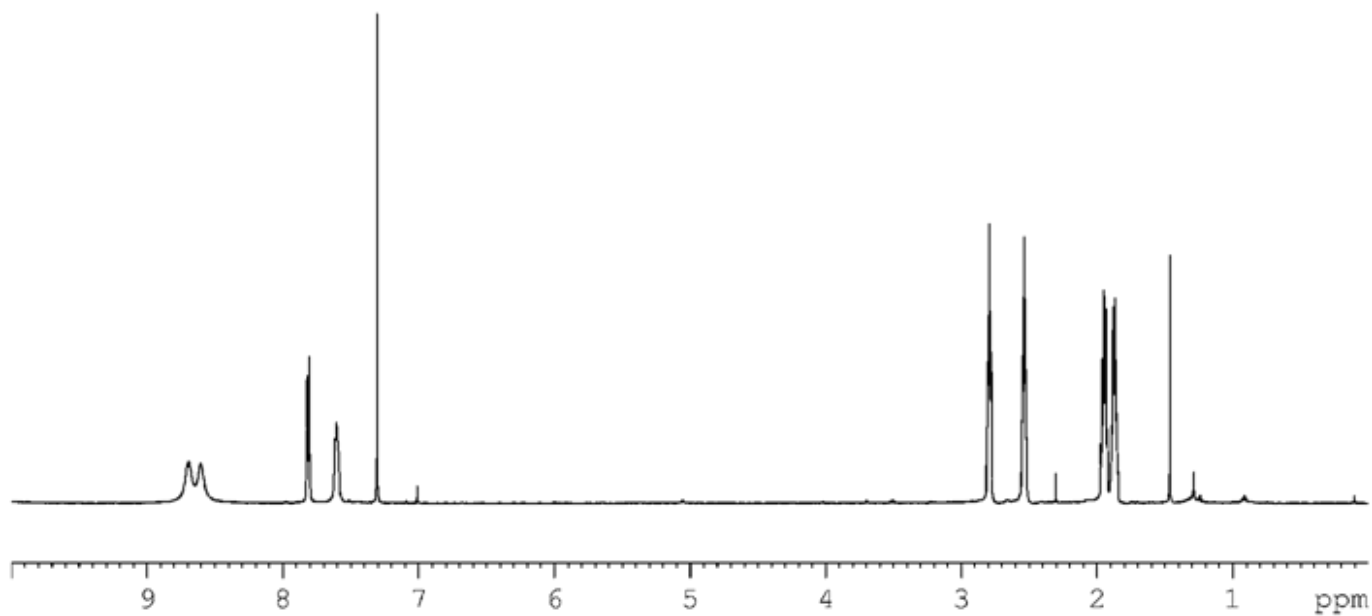


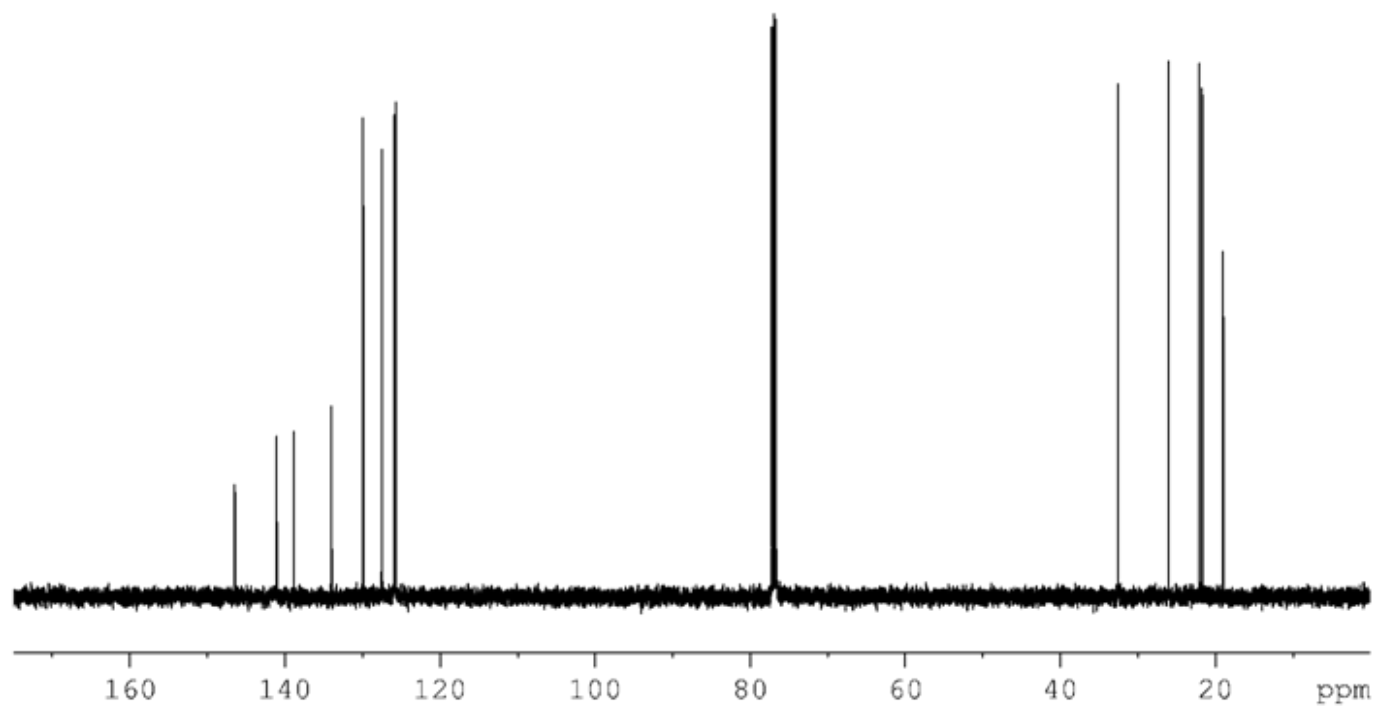
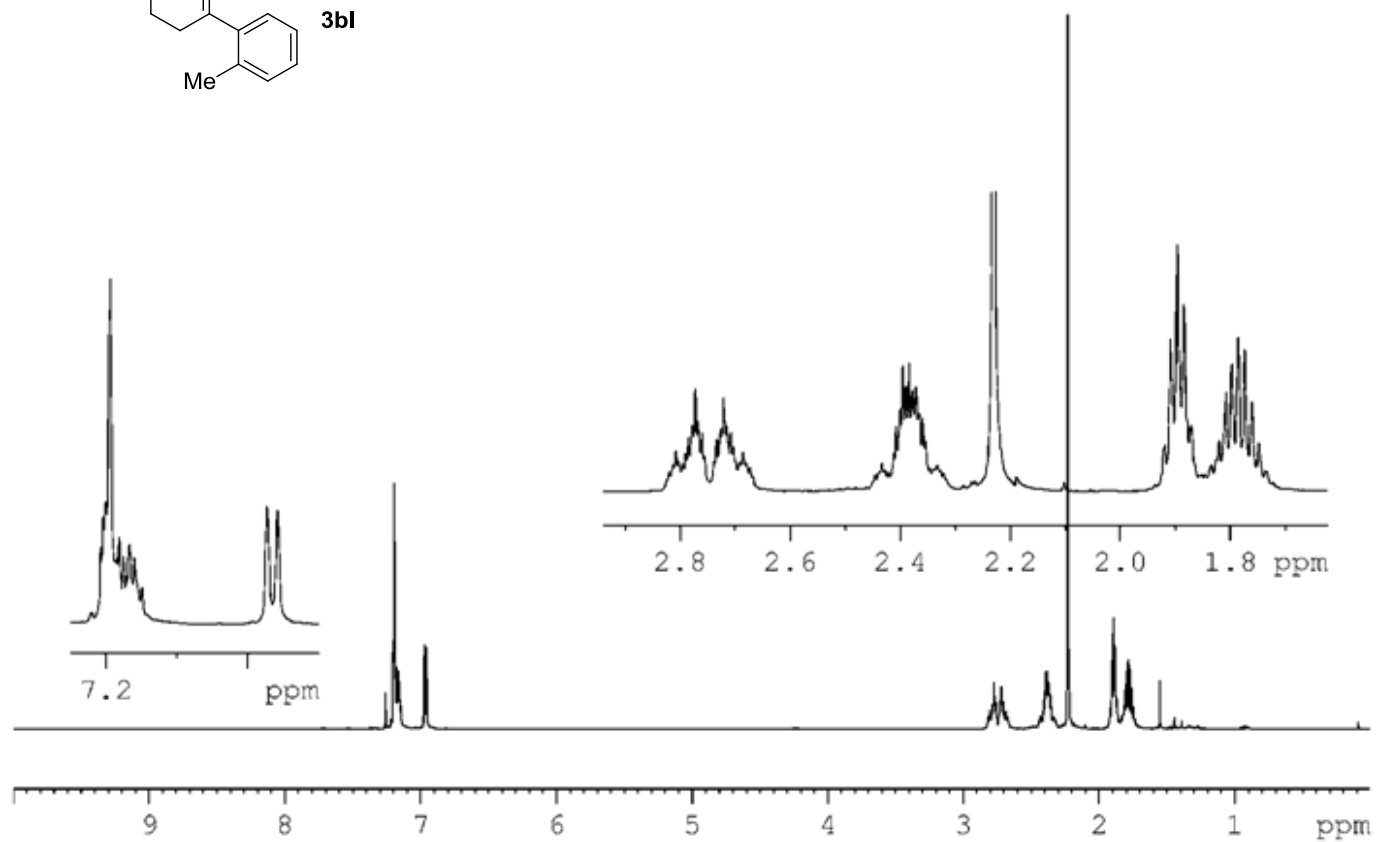
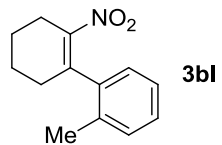




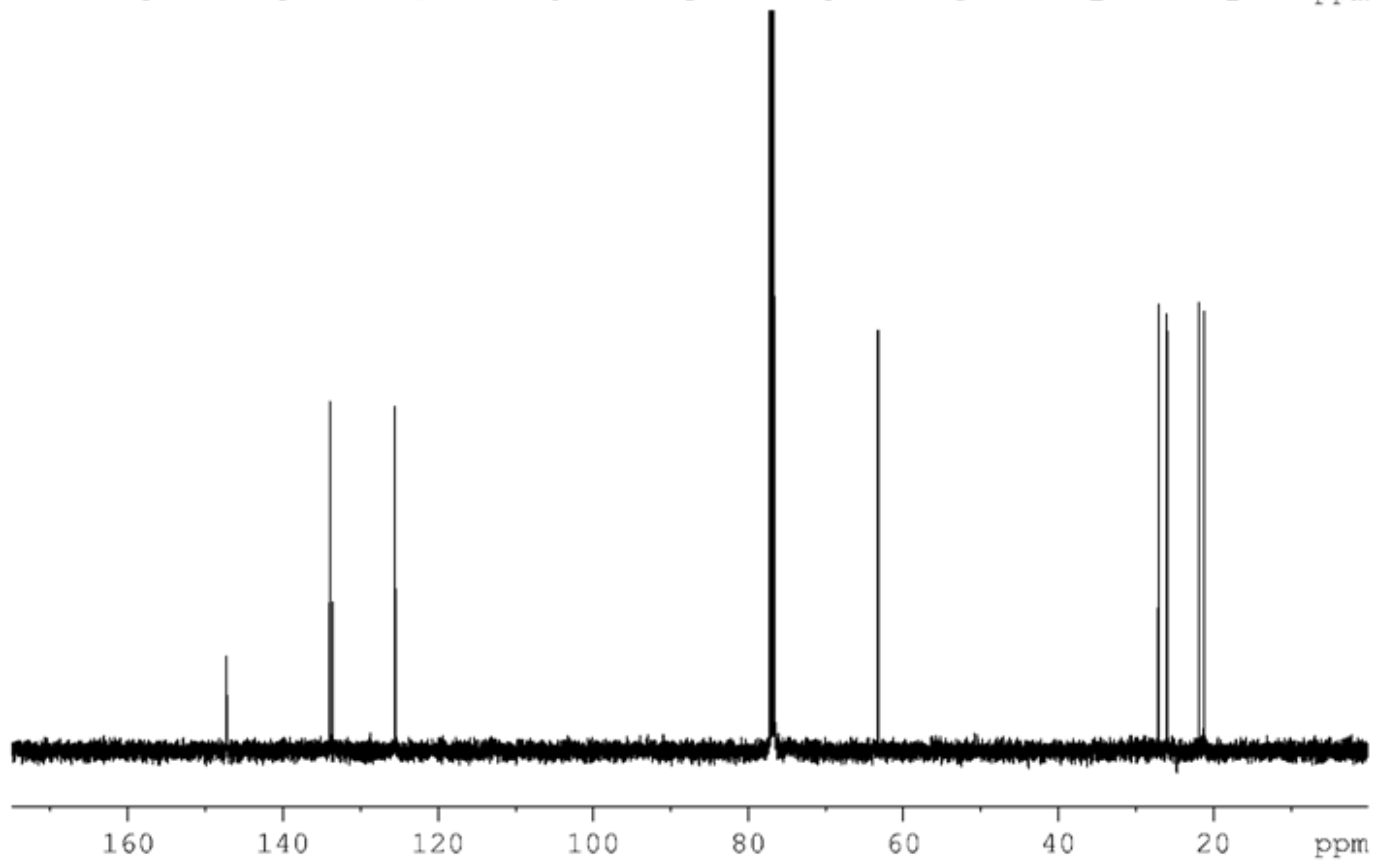
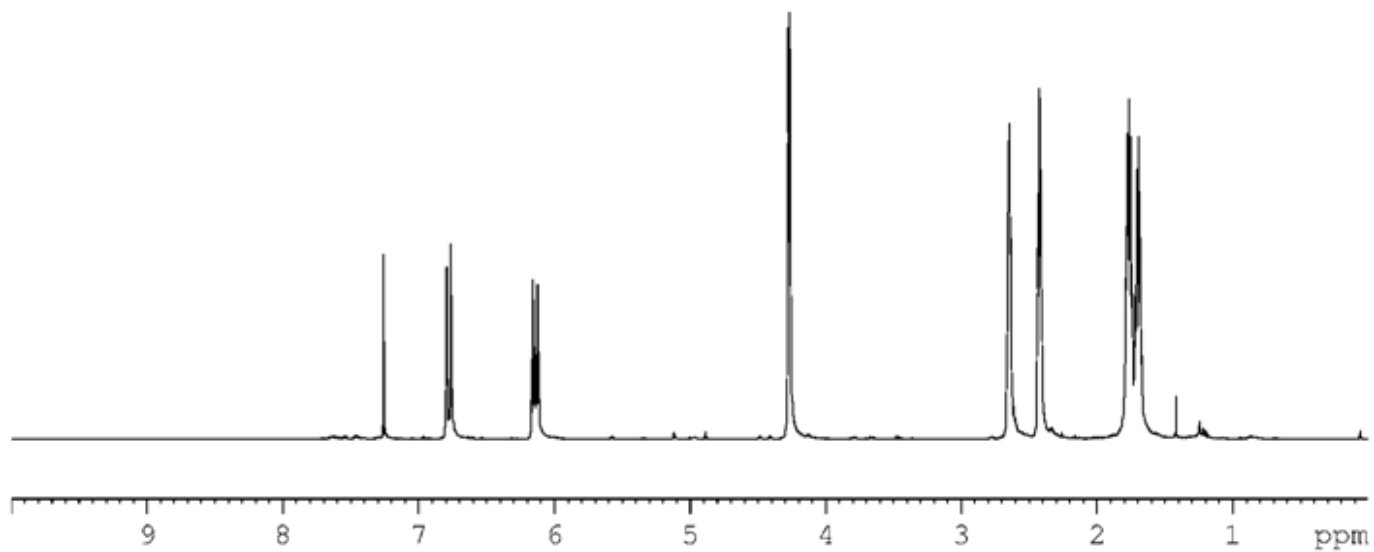
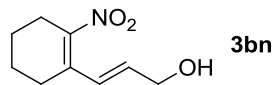


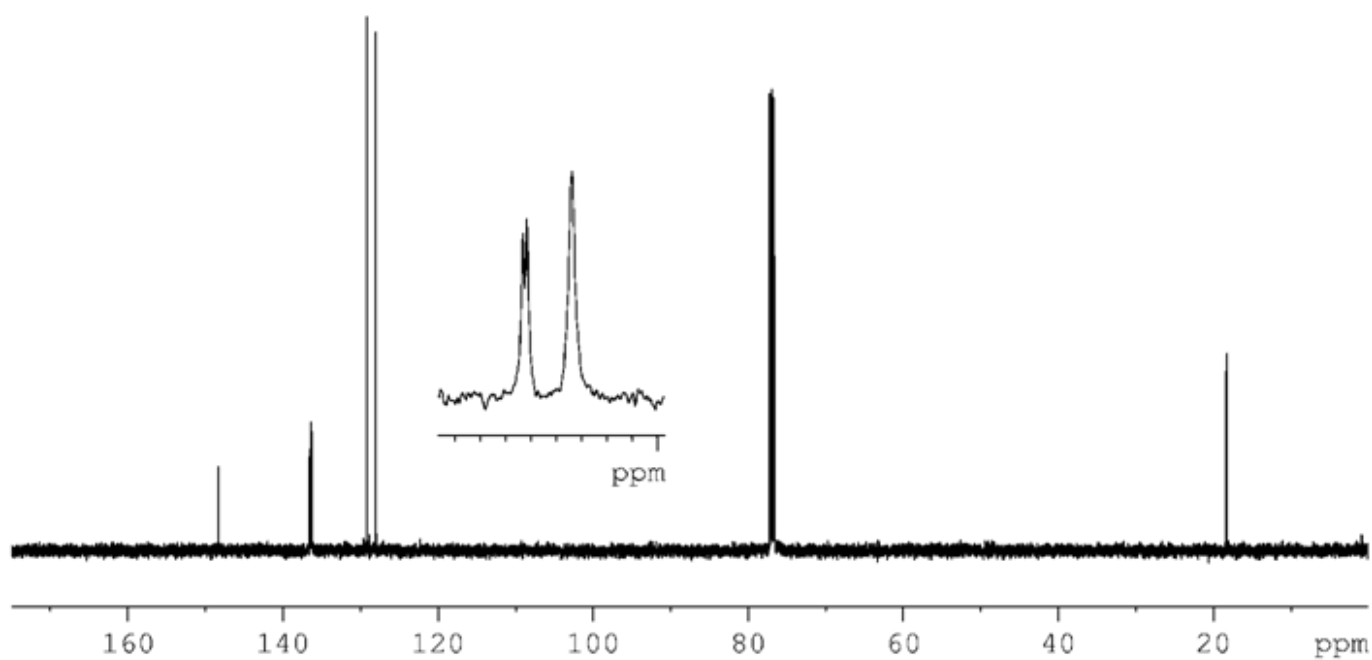
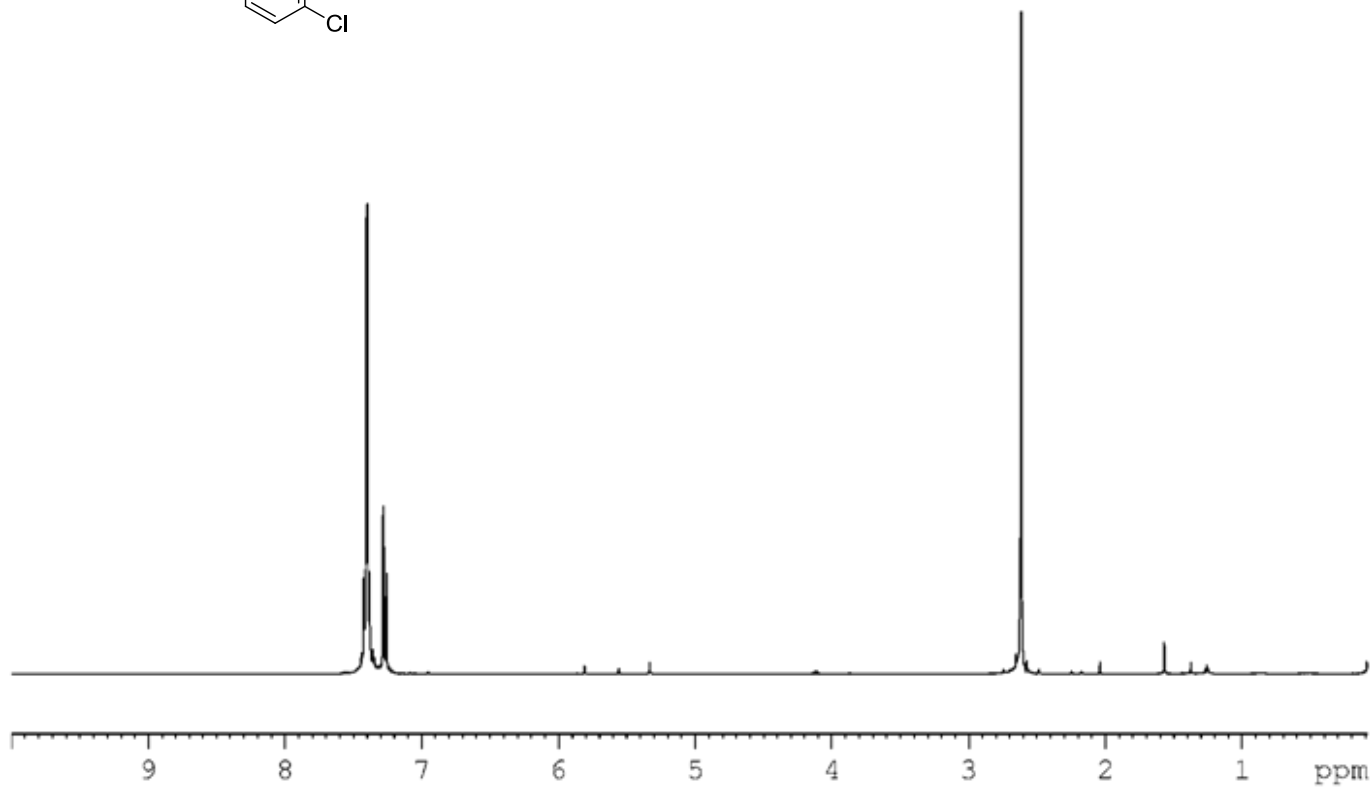
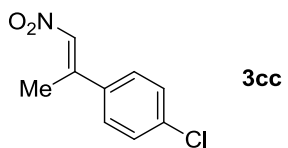
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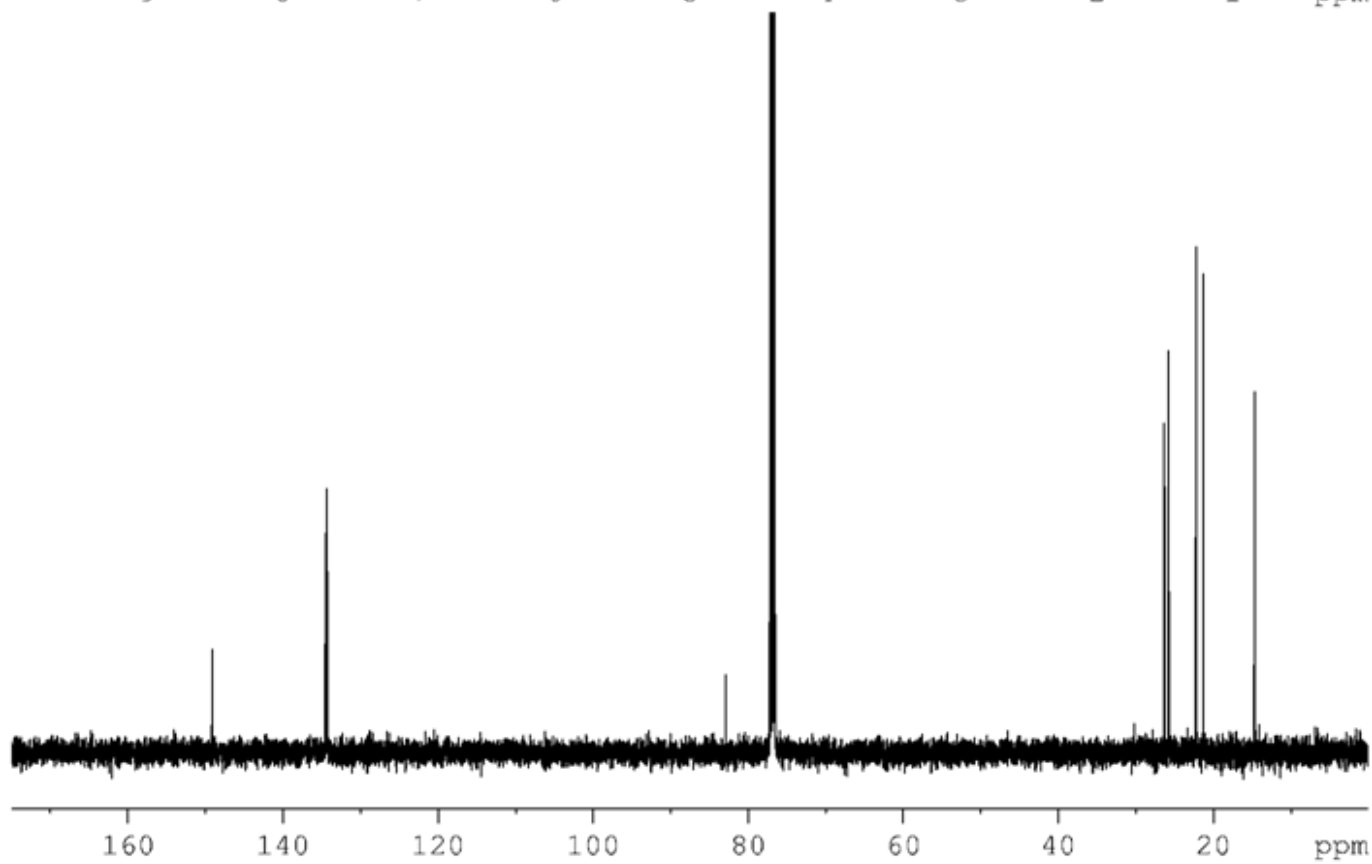
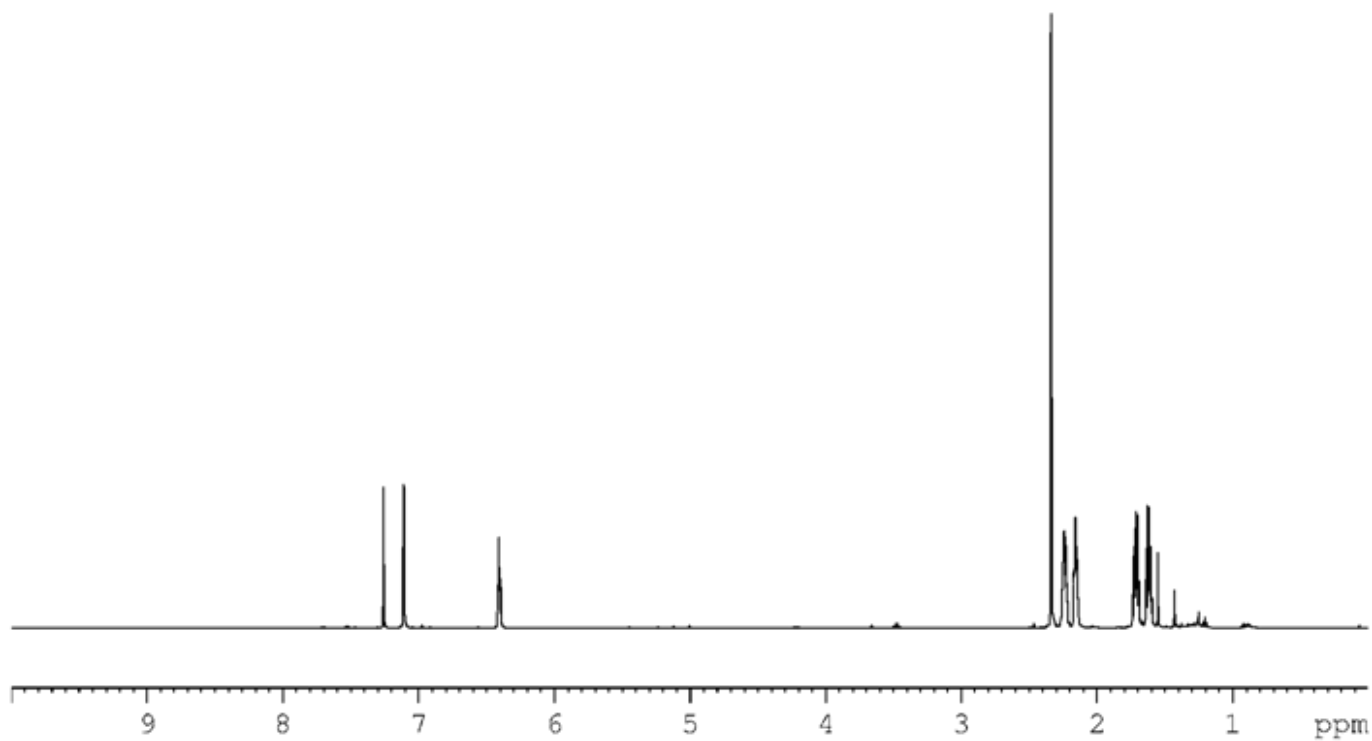
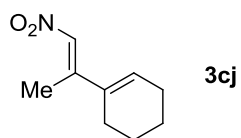


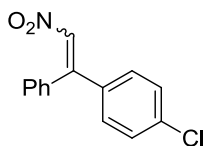












**3dc**

stereochemistry and  
diastereomeric ratio  
not determined

