

**Remarkable Observations on Triplet Sensitized Reactions.  
The Di- $\pi$ -methane Rearrangement of Acyclic 1,4-Dienes in the  
Triplet Excited State.**

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**Supporting Information**

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## Experimental Section

### 1. General

Starting materials and reagents are commercially available unless synthesis is described. The solvents were dried and distilled, before use. Spectral data of the known compounds were in accordance with the literature data. Flash chromatography was performed using silica gel 60 (230-400 mesh).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER AC-200 spectrometer at 200 and 50 MHz, respectively or a BRUKER Avance-AV-500 spectrometer at 500 and 125 MHz, respectively, in  $\text{CDCl}_3$  solution. Chemical shifts ( $\delta$ ) were expressed in parts per million (ppm) relative to tetramethylsilane (TMS), and coupling constants  $J$  were given in hertz (Hz). Infrared spectra were recorded as a thin film using NaCl plate on a PERKIN-ELMER 781 spectrophotometer. UV/visible spectra were recorded on a PERKIN-ELMER LAMBDA 3B apparatus, in  $\text{CH}_2\text{Cl}_2$  solution. Combustion analyses (C, H, N, S) were obtained on a LECO CHNS-932 apparatus at the Universidad Complutense de Madrid analysis services and were within 0.4% of the theoretical values.

### 2. Synthesis of Dienes 4

Dienes **4a**,<sup>1</sup> **4b**,<sup>2</sup> **4c**,<sup>3</sup> **4d**<sup>3</sup> and **4g**<sup>4</sup> were synthesized by the methods previously described. Their spectroscopic data are in agreement with those previously described ( $^1\text{H}$  NMR spectra are shown in pages S13-S21).

Dienes **4e** and **4f** were synthesized from 2-(1,3-dithian-2-yl)-2-methylpropanal<sup>5</sup> (Scheme 1).

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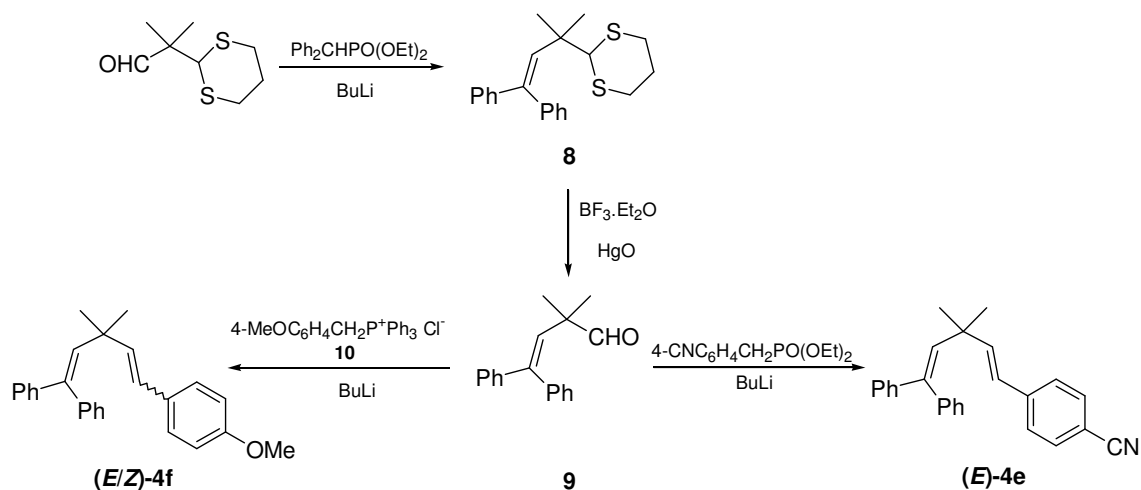
<sup>1</sup> Zimmerman, H. E.; Mariano, P.S. *J. Am. Chem. Soc.* **1969**, *91*, 1718-1727.

<sup>2</sup> Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259-6267.

<sup>3</sup> Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775-1803.

<sup>4</sup> Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131-4145.

<sup>5</sup> Taylor, E. C.; LaMattina, J. L. *Tetrahedron Lett.* **1997**, *24*, 2077-2080.



### Synthesis of 2-(1,1-Dimethyl-3,3-diphenyl-2-propenyl)-1,3-dithiane (**8**).

To a stirred solution of diethyl methyl(diphenyl)phosphonate<sup>3</sup> (6.64 g, 22 mmol) in 30 mL of dry THF, under an argon atmosphere and at 0 °C, was added slowly dropwise BuLi (9 mL, 2.5 M in hexane). The solution was stirred at 0 °C for 1 h and then 2-(1,3-dithian-2-yl)-2-methylpropanal (3.5 g, 18 mmol) in 20 mL of dry THF was added. The reaction mixture was stirred at 0 °C for 3 h before being quenched with saturated NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The combined organic phases were dried, filtered and concentrated to dryness. Flash chromatography using hexane/Et<sub>2</sub>O (98:2) afforded **8** (3.7 g, 61%) as a colorless oil; <sup>1</sup>H NMR (200 MHz) δ 7.32-6.92 (m, 10H), 6.07 (s, 1H), 3.92 (s, 1H), 2.76-2.68 (m, 4H), 2.02-1.89 (m, 1H), 1.82-1.62 (m, 1H), 1.04 (s, 6H); <sup>13</sup>C NMR (50 MHz) δ 144.0, 143.6, 141.0, 140.6, 136.1, 130.2-126.0, 62.2, 42.1, 31.5, 27.3, 26.2; IR (neat) ν 1602 cm<sup>-1</sup>.

### Synthesis of 2,2-Dimethyl-4,4-diphenyl-3-butenal (**9**).

The removal of the thioacetal group was carried out by the method of Vedejs and Fuchs.<sup>6</sup> To a stirred suspension of red mercuric oxide (3.5 g, 16.2 mmol) in 100 mL of 15% aqueous THF under an argon atmosphere, was added BF<sub>3</sub>·Et<sub>2</sub>O (2.3 g, 16.2 mmol). Then, a solution of **8** (3.7 g, 10.8 mmol) in 40 mL of THF was added through a dropping funnel. The stirred mixture was maintained at rt for 20 min and then gently refluxed to complete the reaction. The mixture was allowed to cool to rt and the mercuric salts were precipitated by addition of Et<sub>2</sub>O and then filtered. The filtrate was

<sup>6</sup> Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, 36, 366-367.

washed with saturated NaHCO<sub>3</sub> solution, then with brine and finally dried. The organic phases were concentrated and the residue was purified by flash chromatography using hexane/Et<sub>2</sub>O (98:2) to afford **9**<sup>2</sup> (2.2 g, 81%) as an oil.

**Synthesis of (*E*)-5-(4-Cyanophenyl)-3,3-dimethyl-1,1-diphenyl-1,4-pentadiene (**4e**).**

To a solution of lithium diisopropylamide (2.8 mmol) in dry THF (15 mL), prepared from diisopropylamine (0.4 mL, 2.8 mmol) and BuLi (1.8 mL, 1.6 M in hexane), at –78 °C under an atmosphere of argon, a solution of diethyl 4-cyanophenylmethyl phosphonate<sup>7</sup> (700 mg, 2.8 mmol) in dry THF (10 mL) was added. The mixture was stirred for 1 h and then, a solution of 2,2-dimethyl-4,4-diphenyl-3-butenal (**9**) (630 mg, 2.5 mmol) in dry THF (15 mL) was added dropwise. The reaction was kept at –78 °C for 2 h, allowed to warm to rt and stirred for 24 h before being quenched with a saturated NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The combined organic phases were dried, filtered and concentrated to dryness. Flash chromatography using hexane/Et<sub>2</sub>O (95:5) afforded diene (*E*)-**4e** (783 mg, 89%) as a colorless oil; <sup>1</sup>H NMR (200 MHz) δ 7.39 (dd, *J* = 6.7, 2.0, 2H), 7.22–6.95 (m, 12H), 6.09 (d, *J* = 16.2, 1H), 6.03 (s, 1H), 5.95 (d, *J* = 16.2, 1H), 1.17 (s, 6H); <sup>13</sup>C NMR (50 MHz) δ 143.3, 142.4–137.5, 137.1, 132.3–123.6, 119.1, 109.6, 39.5, 29.2; IR (neat) ν 2228, 1607 cm<sup>–1</sup>; UV (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> 282 nm (ε 21357), 313 nm (ε 2761), 366 (ε 453); MS *m/z* (%) 349 (M<sup>+</sup>, 81), 334 (32), 306 (100), 233 (49), 218 (39), 205 (26), 167 (32), 105 (22), 91 (59), 77 (11).

**Synthesis of 5-(4-Methoxyphenyl)-3,3-dimethyl-1,1-diphenyl-1,4-pentadiene (**4f**).**

To a solution of lithium diisopropylamide (4.3 mmol) in dry THF (30 mL), prepared from diisopropylamine (0.6 mL, 4.3 mmol) and BuLi (4.8 mL, 1.6 M in hexane), at –78 °C under an atmosphere of argon, a solution of 4-methoxyphenylmethyltriphenylphosphonium chloride (**10**)\* (1 g, 4.3 mmol) in dry THF (15 mL) was added dropwise. The mixture was stirred for 1 h and then a solution of 2,2-dimethyl-4,4-diphenyl-3-butenal (**9**) (840 mg, 3.6 mmol) in dry THF (20 mL) was added dropwise. The reaction was kept at –78 °C for 2 h, allowed to warm to rt and stirred for 24 h before being quenched with a saturated NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The combined organic phases were dried, filtered and concentrated to dryness. Flash chromatography using hexane/EtOAc (98:2) afforded diene **4f** (1.1 g,

<sup>7</sup> Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Martín-Fontecha, M. *Org. Lett.* **2005**, 7, 2687–2690.

89%) (*E/Z*; 3:5) as a colorless oil;  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.24-6.67 (m, 14H), 6.06 (d,  $J$  = 12.4, 0.63H, *Z*-isomer), 6.05 (s, 0.37H, *E*-isomer), 6.00 (s, 0.63H, *Z*-isomer), 6.01 (d,  $J$  = 16.4, 0.37H, *E*-isomer), 5.85 (d,  $J$  = 16.4, 0.37H, *E*-isomer), 5.30 (d,  $J$  = 12.4, 0.63H, *Z*-isomer), 3.70 (s, 1.12H, *E*-isomer), 3.66 (s, 1.88H, *Z*-isomer), 1.10 (s, 2.25H, *E*-isomer), 1.02 (s, 3.75H, *Z*-isomer);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  158.7 (*E*-isomer), 158.4 (*Z*-isomer), 144.0-137.8, 130.9-124.6, 113.8 (*E*-isomer), 113.3 (*Z*-isomer), 55.4 (*E*-isomer), 55.3 (*Z*-isomer), 39.4 (*E*-isomer), 39.0 (*Z*-isomer), 31.1 (*Z*-isomer), 29.6 (*E*-isomer); IR (neat)  $\nu$  1606  $\text{cm}^{-1}$ ; UV ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  253 nm ( $\epsilon$  18447), 313 nm ( $\epsilon$  487), 366 nm ( $\epsilon$  216); MS  $m/z$  (%) 354 ( $\text{M}^+$ , 100), 339 (50), 311 (39), 233 (41), 218 (16), 167 (23), 121 (45), 105 (16), 91 (45), 77 (20).

\* This compound was synthesized by refluxing a mixture of triphenylphosphine (25 g, 95 mmol) and 4-methoxybenzyl chloride (14.5 g, 93 mmol) for 3 h. The white precipitate was filtered, washed several times with warmed toluene and hexane and dried to yield 35 g (96%) of **10** (mp > 300 °C);  $^1\text{H}$  NMR (200 MHz)  $\delta$  7.79-7.56 (m, 15H), 6.99 (dd,  $J$  = 8.8, 2.6, 2H), 6.62 (d,  $J$  = 8.4, 2H), 5.34 (d,  $J$  = 14.8, 2H), 3.70 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz)  $\delta$  159.5, 134.8-129.9, 118.8, 117.2, 114.1, 55.2, 30.0.

### 3. General Procedure for Preparative Photolyses of Dienes **4a-4g**.

The photolyses were carried out in a quartz immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. Solutions of the compound, the sensitizer (in the sensitized irradiations) and the solvent ( $\text{CH}_2\text{Cl}_2$ ) were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent and the sensitizer (acetophenone or 3-methoxyacetophenone) were removed under reduced pressure. The products and the sensitizers (thioxanthone, 4-phenylbenzophenone and chrysene) were separated by flash chromatography on silica gel.

Spectroscopic data of known compounds (**5a**,<sup>1</sup> **5b**,<sup>2</sup> **5c**,<sup>3</sup> **5d**,<sup>3</sup> and **5g**<sup>4</sup>) are in agreement with those previously described ( $^1\text{H}$  NMR spectra are shown in pages S22-S34).

**3-Methoxyacetophenone-Sensitized Irradiation of 4a.** Compound **4a** (200 mg, 0.5 mmol) and 3-methoxyacetophenone (1.3 mL, 8.7 mmol) in  $\text{CH}_2\text{Cl}_2$  (160 mL) were irradiated for 4 h. Chromatography using hexane/ $\text{Et}_2\text{O}$  (99:1) as eluent gave starting diene **4a** (186 mg, 93%) and vinylcyclopropane **5a**<sup>1</sup> (8 mg, 4%). Further elution with

Et<sub>2</sub>O afforded 4 mg of highly polar material.

**Thioxanthone-Sensitized Irradiation of 4a.** Compound **4a** (200 mg, 0.5 mmol) and thioxanthone (150 mg, 0.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 4 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4a** (142 mg, 71%) and vinylcyclopropane **5a** (30 mg, 15%). Further elution with Et<sub>2</sub>O afforded 10 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4a.** Compound **4a** (200 mg, 0.5 mmol) and 4-phenylbenzophenone (254 mg, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 4 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4a** (144 mg, 72%) and vinylcyclopropane **5a** (50 mg, 25%). Further elution with Et<sub>2</sub>O afforded 4 mg of highly polar material.

**Chrysene-Sensitized Irradiation of 4a.** Compound **4a** (200 mg, 0.5 mmol) and chrysene (150 mg, 0.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 4 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4a** (140 mg, 70%) and vinylcyclopropane **5a** (30 mg, 15%). Further elution with Et<sub>2</sub>O afforded 15 mg of highly polar material.

**Acetophenone-Sensitized Irradiation of 4b.** Compound **4b** (200 mg, 0.72 mmol) and acetophenone (42 mL, 359 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4b** (76 mg, 38%) and vinylcyclopropane **5b**<sup>2</sup> (86 mg, 43%). Further elution with Et<sub>2</sub>O afforded 27 mg of highly polar material.

**3-Methoxyacetophenone-Sensitized Irradiation of 4b.** Compound **4b** (200 mg, 0.72 mmol) and 3-methoxyacetophenone (14 mL, 9.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4b** (96 mg, 48%) and vinylcyclopropane **5b** (76 mg, 38%). Further elution with Et<sub>2</sub>O afforded 18 mg of highly polar material.

**Thioxanthone-Sensitized Irradiation of 4b.** Compound **4b** (200 mg, 0.72 mmol) and thioxanthone (191 mg, 0.90 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4b** (6 mg, 3%) and vinylcyclopropane **5b** (160 mg, 80%). Further elution with Et<sub>2</sub>O afforded 29 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4b.** Compound **4b** (200 mg, 0.72 mmol) and 4-phenylbenzophenone (243 mg, 0.94 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4b** (105

mg, 52%) and vinylcyclopropane **5b** (94 mg, 47%). Further elution with Et<sub>2</sub>O afforded 1 mg of highly polar material.

**Chrysene-Sensitized Irradiation of 4b.** Compound **4b** (200 mg, 0.72 mmol) and chrysene (252 mg, 1.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4b** (166 mg, 83%). Further elution with Et<sub>2</sub>O afforded 29 mg of highly polar material.

**Acetophenone-Sensitized Irradiation of 4c.** Compound **4c** (182 mg, 0.73 mmol) and acetophenone (0.8 mg, 7.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4c** (124 mg, 68%) and vinylcyclopropane **5c**<sup>3</sup> (22 mg, 12%). Further elution with Et<sub>2</sub>O afforded 25 mg of highly polar material.

**3-Methoxyacetophenone-Sensitized Irradiation of 4c.** Compound **4c** (190 mg, 0.77 mmol) and 3-methoxyacetophenone (0.3 mL, 1.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4c** (97 mg, 51%) and vinylcyclopropane **5c** (68 mg, 36%). Further elution with Et<sub>2</sub>O afforded 15 mg of highly polar material.

**Thioxanthone-Sensitized Irradiation of 4c.** Compound **4c** (200 mg, 0.8 mmol) and thioxanthone (232 mg, 1.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4c** (90 mg, 45%) and vinylcyclopropane **5c** (78 mg, 39%). Further elution with Et<sub>2</sub>O afforded 18 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4c.** Compound **4c** (200 mg, 0.8 mmol) and 4-phenylbenzophenone (97 mg, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4c** (98 mg, 49%) and vinylcyclopropane **5c** (98 mg, 49%). Further elution with Et<sub>2</sub>O afforded 2 mg of highly polar material.

**Chrysene-Sensitized Irradiation of 4c.** Compound **4c** (200 mg, 0.8 mmol) and chrysene (52 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane as eluent gave starting diene **4c** (162 mg, 81%) and vinylcyclopropane **5c** (18 mg, 9%). Further elution with Et<sub>2</sub>O afforded 10 mg of highly polar material.

**Acetophenone-Sensitized Irradiation of 4d.** Compound (*E*)-**4d** (200 mg, 0.73 mmol) and acetophenone (1.3 mL, 11.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave diene **4d** (194 mg, 97%) as a

1:1 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 2 mg of highly polar material.

**3-Methoxyacetophenone-Sensitized Irradiation of 4d.** Compound (*E*)-**4d** (200 mg, 0.73 mmol) and 3-methoxyacetophenone (0.3 mL, 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave diene **4d** (78 mg, 39%) as a 1:1 mixture of *E/Z* isomers, vinylcyclopropane (*Z*)-**5d**<sup>2</sup> (75 mg, 38%) and vinylcyclopropane (*E*)-**5d**<sup>3</sup> (19 mg, 9%). Further elution with Et<sub>2</sub>O afforded 10 mg of highly polar material.

**Thioxanthone-Sensitized Irradiation of 4d.** Compound (*E*)-**4d** (200 mg, 0.73 mmol) and thioxanthone (100 mg, 0.47 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave diene **4d** (4 mg, 2%) as a 1:1 mixture of *E/Z* isomers, vinylcyclopropane (*Z*)-**5d** (60 mg, 30%) and vinylcyclopropane (*E*)-**5d** (118 mg, 59%). Further elution with Et<sub>2</sub>O afforded 5 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4d.** Compound (*E*)-**4d** (200 mg, 0.73 mmol) and 4-phenylbenzophenone (193 mg, 0.70 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave diene **4d** (100 mg, 50%) as a 9:1 mixture of *E/Z* isomers, vinylcyclopropane (*Z*)-**5d** (10 mg, 5%) and vinylcyclopropane (*E*)-**5d** (50 mg, 25%). Further elution with Et<sub>2</sub>O afforded 15 mg of highly polar material.

**Chrysene-Sensitized Irradiation of 4d.** Compound (*E*)-**4d** (200 mg, 0.73 mmol) and chrysene (52 mg, 0.23 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave diene **4d** (160 mg, 83%) as a 5:4 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 25 mg of highly polar material.

**Direct Irradiation of 4e.** Compound (*E*)-**4e** (150 mg, 0.43 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) was irradiated for 45 min. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene (*E*)-**4e** (32 mg, 21%) and vinylcyclopropane (*E*)-**7** (116 mg, 77%) as a colorless oil. Further elution with Et<sub>2</sub>O afforded 2 mg of highly polar material.

Compound (*E*)-**7**: <sup>1</sup>H NMR (200 MHz) δ 7.46-7.01 (m, 14H), 5.84 (d, *J* = 9.0, 1H), 2.00 (d, *J* = 5.8, 1H), 1.79 (dd, *J* = 9.0, 5.8, 1H), 1.31 (s, 3H), 0.73 (s, 3H); <sup>13</sup>C NMR (50 MHz) δ 145.0-140.0, 137.9, 131.8, 131.6-123.5, 118.9, 109.3, 39.3, 31.5, 28.1, 22.8, 21.1; IR (neat) ν 2226, 1607 cm<sup>-1</sup>; MS *m/z* (%) 349 (M<sup>+</sup>, 100), 334 (31), 306 (59), 256



(22), 218 (23), 191 (20), 178 (16), 167 (32), 115 (26), 105 (20), 91 (68), 77 (12). **Acetophenone-Sensitized Irradiation of 4e.** Compound (*E*)-**4e** (209 mg, 0.60 mmol) and acetophenone (45 mL, 384 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (450 mL) were irradiated for 90 min. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene (*E*)-**4e** (184 mg, 88%). Further elution with Et<sub>2</sub>O afforded 20 mg of highly polar material.

**3-Methoxyacetophenone-Sensitized Irradiation of 4e.** Compound (*E*)-**4e** (150 mg, 0.43 mmol) and 3-methoxyacetophenone (10 mL, 68.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 90 min. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene (*E*)-**4e** (103 mg, 69%) and vinylcyclopropane (*E*)-**5e** (30 mg, 20%) as a colorless oil. Further elution with Et<sub>2</sub>O afforded 10 mg of highly polar material.

Compound (*E*)-**5e**: <sup>1</sup>H NMR (200 MHz) δ 7.47 (d, *J* = 8.4, 2H), 7.34-7.00 (m, 12H), 6.63 (d, *J* = 15.7, 1H), 5.89 (dd, *J* = 15.7, 10.3, 1H), 2.20 (d, *J* = 10.3, 1H), 1.19 (s, 3H), 1.03 (s, 3H); <sup>13</sup>C NMR (50 MHz) δ 145.2-141.5, 134.6-126.2, 119.3, 109.7, 77.3, 47.8, 38.9, 25.9, 20.7; IR (neat) ν 2228, 1602 cm<sup>-1</sup>; MS *m/z* (%) 349 (M<sup>+</sup>, 32), 306 (100), 233 (18), 165 (24), 105 (10), 91 (26).

**Thioxanthone-Sensitized Irradiation of 4e.** Compound (*E*)-**4e** (250 mg, 0.72 mmol) and thioxanthone (817 mg, 3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 90 min. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene (*E*)-**4e** (186 mg, 75%) and vinylcyclopropane (*E*)-**5e** (45 mg, 18%). Further elution with Et<sub>2</sub>O afforded 16 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4e.** Compound (*E*)-**4e** (220 mg, 0.63 mmol) and 4-phenylbenzophenone (1.1 g, 4.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 90 min. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene (*E*)-**4e** (88 mg, 40%) and vinylcyclopropane (*E*)-**5e** (121 mg, 55%). Further elution with Et<sub>2</sub>O afforded 5 mg of highly polar material.

**Chrysene-Sensitized Irradiation of 4e.** Compound (*E*)-**4e** (210 mg, 0.60 mmol) and chrysene (271 mg, 1.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 90 min. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene (*E*)-**4e** (178 mg, 85%) and vinylcyclopropane (*E*)-**5e** (17 mg, 8%). Further elution with Et<sub>2</sub>O afforded 10 mg of highly polar material.

**Direct Irradiation of 4f.** Compound **4f** (180 mg, 0.51 mmol) as a 3:5 mixture of *E/Z* isomers in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) was irradiated for 2.5 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4f** (97 mg, 54%) as a 3:2 mixture of

*E/Z* isomers and vinylcyclopropane **5f** (40 mg, 22%) as a 1:1 mixture of *E/Z* isomers and as a colorless oil. Further elution with Et<sub>2</sub>O afforded 35 mg of highly polar material. Compound **5f**: <sup>1</sup>H NMR (500 MHz) δ 7.45-7.09 (m, 12H), 6.95 (d, *J* = 10.0, 1H, *E*-isomer), 6.87 (d, *J* = 10.0, 1H, *Z*-isomer), 6.68 (d, *J* = 15.0, 0.5H, *E*-isomer), 6.52 (d, *J* = 10.0, 0.5H, *Z*-isomer), 5.65 (dd, *J* = 15.0, 10.0, 0.5H, *E*-isomer), 5.25 (t, *J* = 10.0, 0.5H, *Z*-isomer), 3.87 (s, 1.5H, *Z*-isomer), 3.82 (s, 1.5H, *E*-isomer), 2.54 (d, *J* = 10.0, 0.5H, *Z*-isomer), 2.26 (d, *J* = 10.0, 0.5H, *E*-isomer), 1.25 (s, 1.5H, *E*-isomer), 1.21 (s, 1.5H, *Z*-isomer), 1.14 (s, 1.5H, *E*-isomer), 1.11 (s, 1.5H, *Z*-isomer); <sup>13</sup>C NMR (125 MHz) δ 159.0, 158.7, 148.2, 145.9, 142.3, 141.7, 138.4, 138.1, 131.8-124.9, 114.3, 114.1, 55.8, 55.7, 46.8, 46.7, 39.7, 39.0, 34.0, 29.9, 28.9, 28.6, 26.3, 26.0, 21.2, 21.0; IR (neat) ν 2228, 1614 cm<sup>-1</sup>; MS *m/z* (%) 354 (M<sup>+</sup>, 100), 330 (42), 311 (38), 233 (40), 121 (44), 91 (45), 77 (19).

**Acetophenone-Sensitized Irradiation of 4f.** Compound **4f** (170 mg, 0.48 mmol) as a 3:5 mixture of *E/Z* isomers and acetophenone (6 mL, 54.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (450 mL) were irradiated for 2 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4f** (136 mg, 80%) as a 2:1 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 28 mg of highly polar material.

**3-Methoxyacetophenone-Sensitized Irradiation of 4f.** Compound **4f** (170 mg, 0.48 mmol) as a 3:5 mixture of *E/Z* isomers and 3-methoxyacetophenone (2.7 mL, 18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 2 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4f** (80 mg, 47%) as a 10:1 mixture of *E/Z* isomers and vinylcyclopropane **5f** (68 mg, 40%) as a 1:1 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 18 mg of highly polar material.

**Thioxanthone-Sensitized Irradiation of 4f.** Compound **4f** (180 mg, 0.51 mmol) as a 3:5 mixture of *E/Z* isomers and thioxanthone (553 mg, 2.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 2 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4f** (135 mg, 75%) as a 10:1 mixture of *E/Z* isomers and vinylcyclopropane **5f** (18 mg, 10%) as a 1:1 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 20 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4f.** Compound **4f** (200 mg, 0.56 mmol) as a 3:5 mixture of *E/Z* isomers and 4-phenylbenzophenone (748 mg, 2.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 2 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4f** (96 mg, 48%) as a 10:1 mixture of *E/Z* isomers and

vinylcyclopropane **5f** (76 mg, 38%) as a 1:1 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 22 mg of highly polar material.

**Chrysene-Sensitized Irradiation of 4f.** Compound **4f** (210 mg, 0.59 mmol) as a 3:5 mixture of *E/Z* isomers and chrysene (210 mg, 0.92 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 2 h. Chromatography using hexane/Et<sub>2</sub>O (99:1) as eluent gave starting diene **4f** (145 mg, 69%) as a 10:1 mixture of *E/Z* isomers and vinylcyclopropane **5f** (53 mg, 25%) as a 1:1 mixture of *E/Z* isomers. Further elution with Et<sub>2</sub>O afforded 5 mg of highly polar material.

**Acetophenone-Sensitized Irradiation of 4g.** Compound **4g** (140 mg, 0.27 mmol) and acetophenone (32 mL, 268 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (160 mL) were irradiated for 3 h. Chromatography using hexane/EtOAc (98:2) as eluent gave starting diene **4g** (98 mg, 70%) and vinylcyclopropane **5g**<sup>4</sup> (20 mg, 14%). Further elution with Et<sub>2</sub>O afforded 18 mg of highly polar material.

**3-Methoxyacetophenone-Sensitized Irradiation of 4g.** Compound **4g** (200 mg, 0.39 mmol) and 3-methoxyacetophenone (7 mL, 47 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane/EtOAc (98:2) as eluent gave starting diene **4g** (108 mg, 54%) and vinylcyclopropane **5g** (60 mg, 30%). Further elution with Et<sub>2</sub>O afforded 25 mg of highly polar material.

**Thioxanthone-Sensitized Irradiation of 4g.** Compound **4g** (200 mg, 0.39 mmol) and thioxanthone (828 mg, 3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane/EtOAc (98:2) as eluent gave starting diene **4g** (180 mg, 90%). Further elution with Et<sub>2</sub>O afforded 5 mg of highly polar material.

**4-Phenylbenzophenone-Sensitized Irradiation of 4g.** Compound **4g** (200 mg, 0.4 mmol) and 4-phenylbenzophenone (1 g, 3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane/EtOAc (98:2) as eluent gave starting diene **4g** (112 mg, 56%) and vinylcyclopropane **5g** (72 mg, 36%). Further elution with Et<sub>2</sub>O afforded 6 mg of highly polar material.

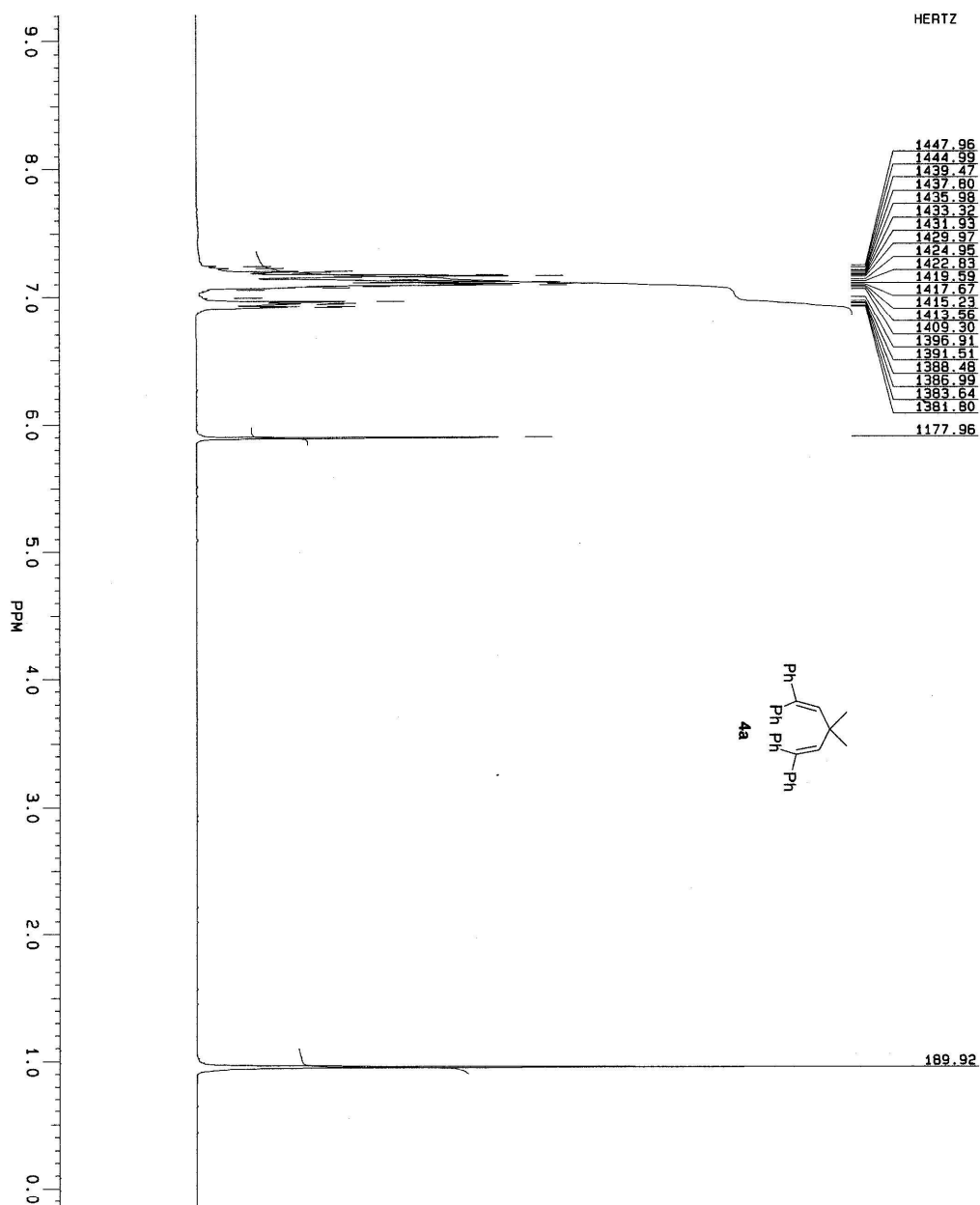
**Chrysene-Sensitized Irradiation of 4g.** Compound **4g** (206 mg, 0.4 mmol) and chrysene (276 mg, 1.21 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were irradiated for 3 h. Chromatography using hexane/EtOAc (98:2) as eluent gave starting diene **4g** (41 mg, 20%) and vinylcyclopropane **5g** (150 mg, 73%). Further elution with Et<sub>2</sub>O afforded 8 mg of highly polar material.

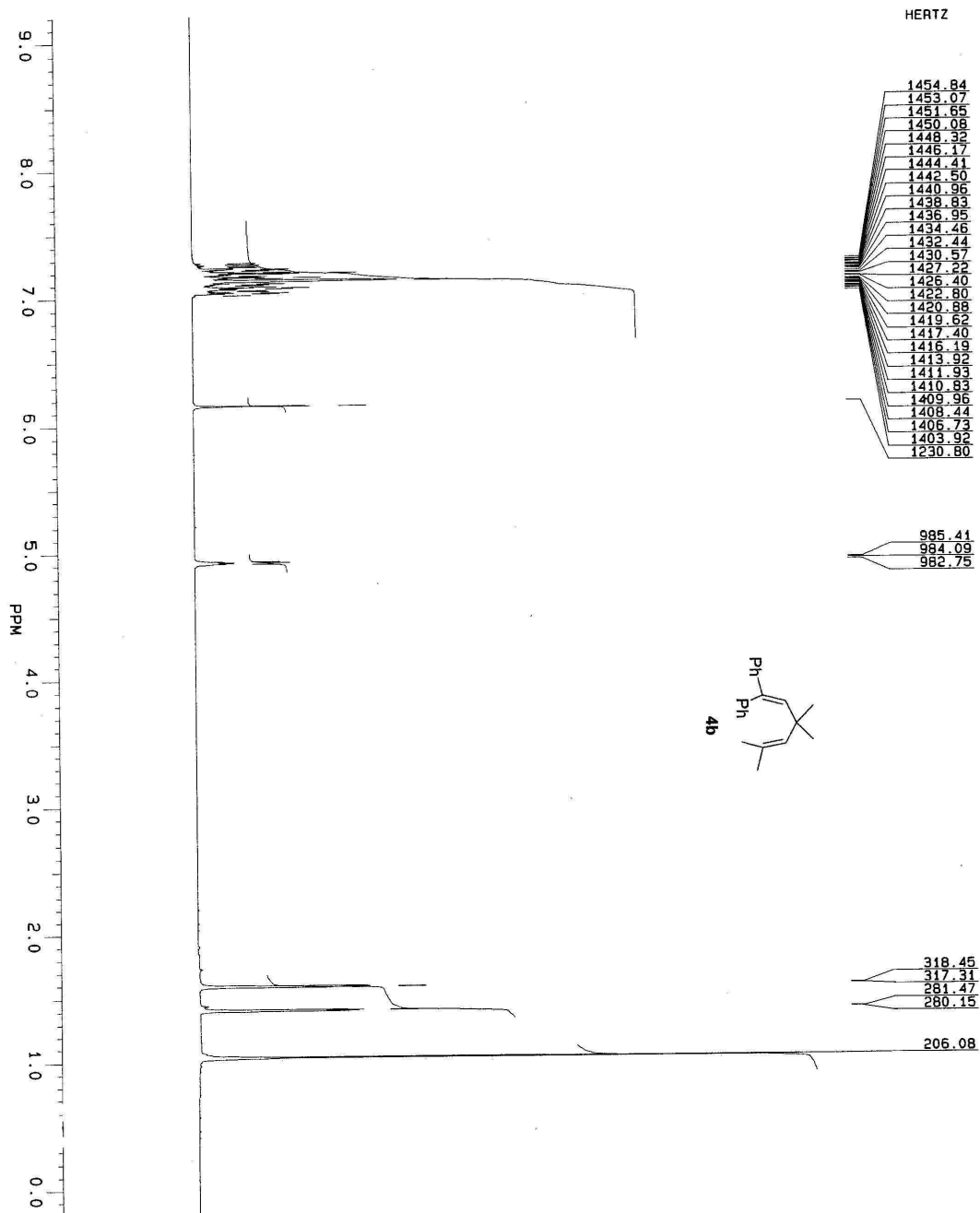
# Combustion Analysis Data

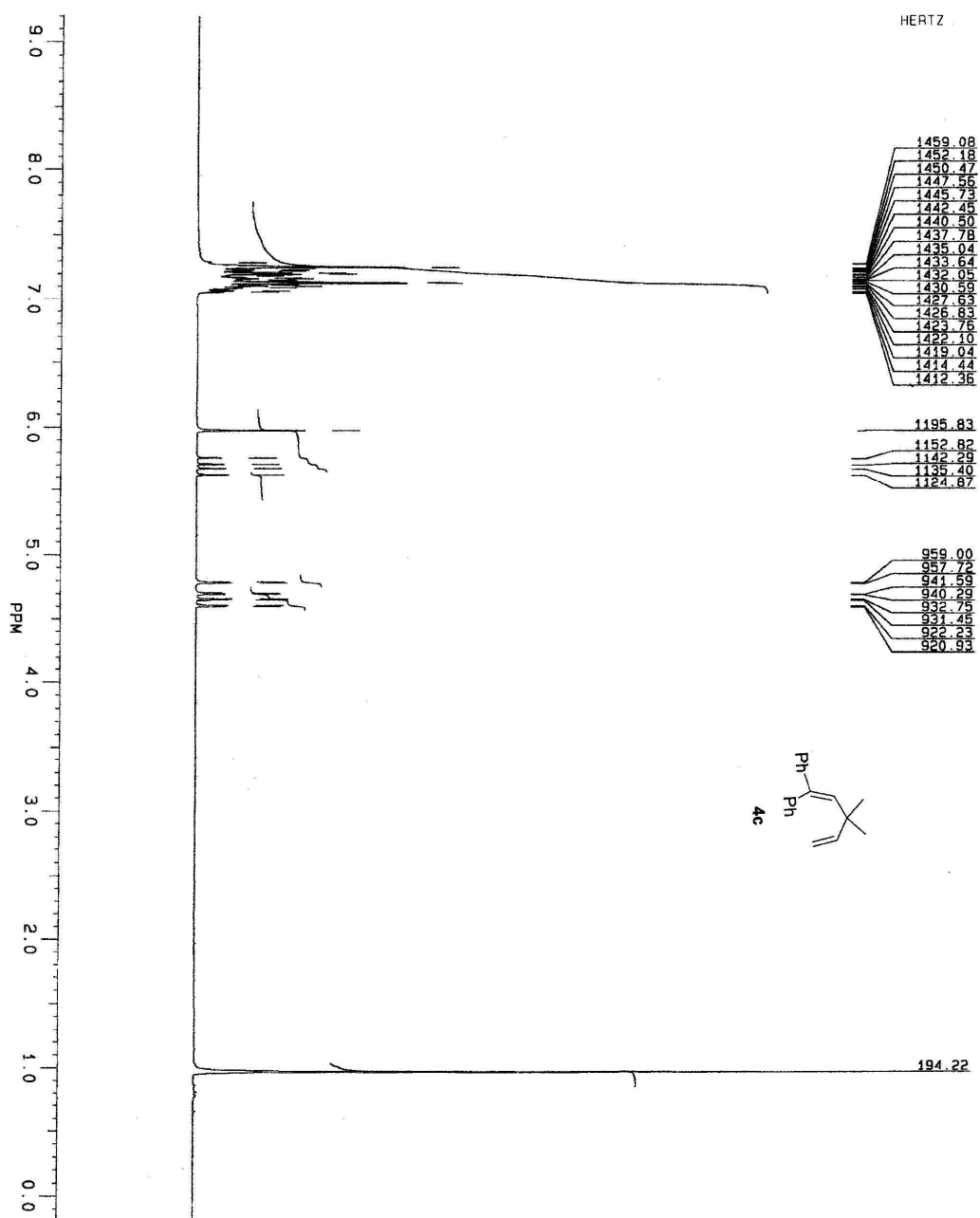
Compd	Molecular Formula	Calculated				Found			
		C	H	N	S	C	H	N	S
<b>4a</b>	C <sub>31</sub> H <sub>28</sub>	92.95	7.05			92.85	7.10		
<b>4b</b>	C <sub>21</sub> H <sub>24</sub>	91.25	8.75			91.08	8.59		
<b>4c</b>	C <sub>19</sub> H <sub>20</sub>	91.88	8.12			91.64	8.23		
<b>(E)-4d</b>	C <sub>20</sub> H <sub>19</sub> N	88.87	7.01	5.12		88.57	7.13	4.98	
<b>(E)-4e</b>	C <sub>26</sub> H <sub>23</sub> N	89.36	6.63	4.01		89.25	6.73	4.00	
<b>4f</b>	C <sub>26</sub> H <sub>26</sub> O	88.09	7.39			87.90	7.42		
<b>4g</b>	C <sub>35</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub>	82.33	5.92	5.49		82.07	6.07	5.57	
<b>5a</b>	C <sub>31</sub> H <sub>28</sub>	92.95	7.05			93.19	7.20		
<b>5b</b>	C <sub>21</sub> H <sub>24</sub>	91.25	8.75			91.39	8.79		
<b>5c</b>	C <sub>19</sub> H <sub>20</sub>	91.88	8.12			91.97	7.93		
<b>(E)-5d</b>	C <sub>20</sub> H <sub>19</sub> N	88.87	7.01	5.12		88.95	7.23	5.28	
<b>(E)-5e</b>	C <sub>26</sub> H <sub>23</sub> N	89.36	6.63	4.01		89.30	6.68	4.00	
<b>5f</b>	C <sub>26</sub> H <sub>26</sub> O	88.09	7.39			88.15	7.38		
<b>5g</b>	C <sub>35</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub>	82.33	5.92	5.49		82.57	6.16	5.57	
<b>7</b>	C <sub>26</sub> H <sub>23</sub> N	89.36	6.63	4.01		89.20	6.70	4.06	
<b>8</b>	C <sub>21</sub> H <sub>24</sub> S <sub>2</sub>	74.06	7.10		18.83	73.95	7.14		18.91
<b>9</b>	C <sub>18</sub> H <sub>18</sub> O	86.36	7.25			86.25	7.20		
<b>10</b>	C <sub>26</sub> H <sub>24</sub> ClOP	74.55	5.77			74.25	6.01		



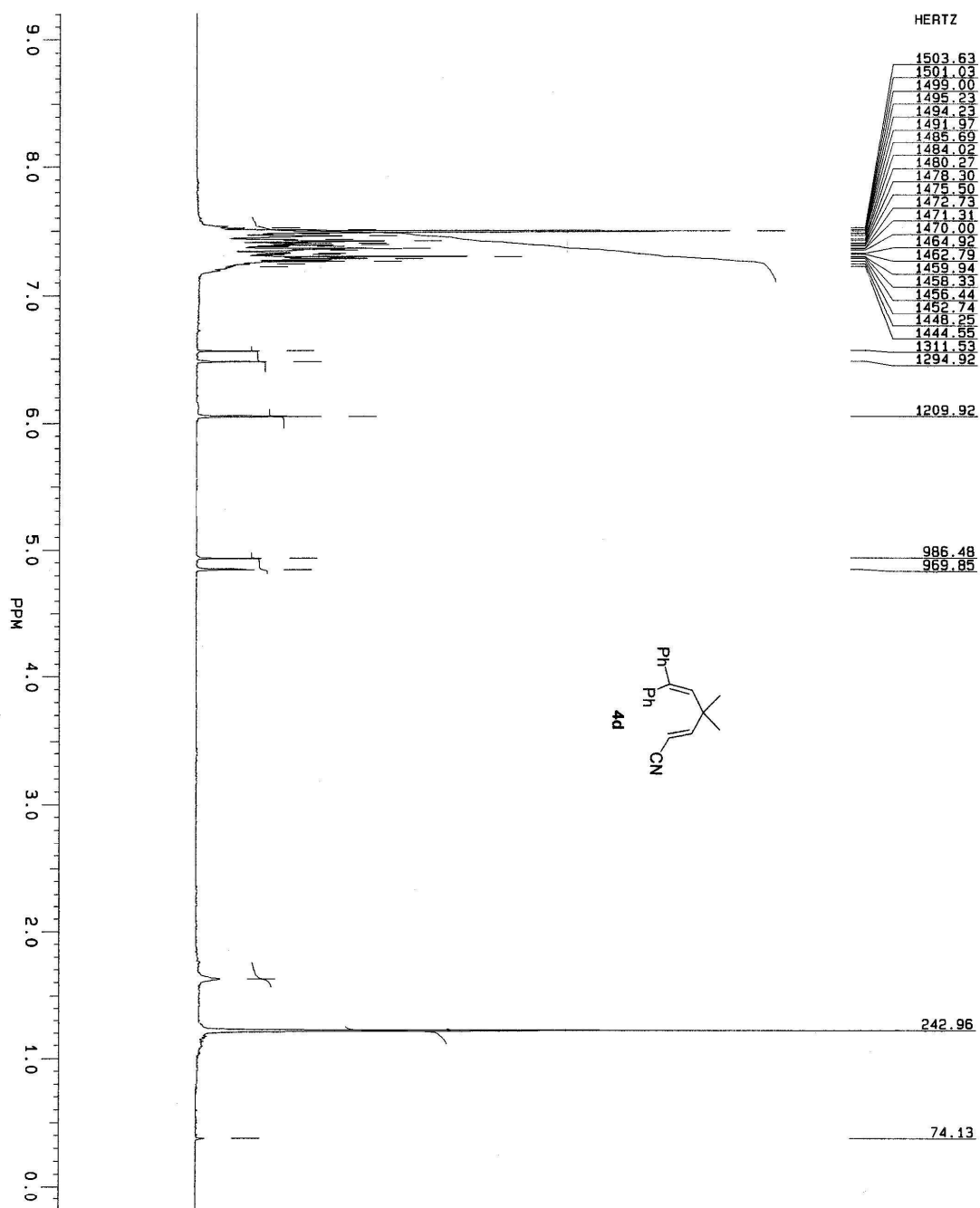
# <sup>1</sup>H and <sup>13</sup>C NMR spectra







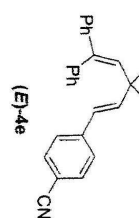




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HERTZ

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1182.31



234.06

