

*Supporting Information for:*

***An Exclusive Approach to 3,4-Disubstituted Cyclopentenenes and Alkylidene Cyclopentenenes via Palladium Catalyzed Ring  
Opening of Azabicyclic olefins with Aryl halides***

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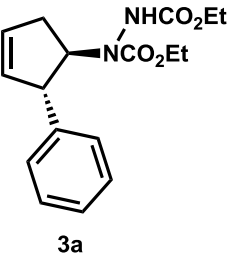
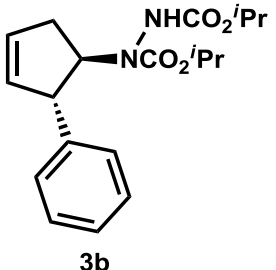
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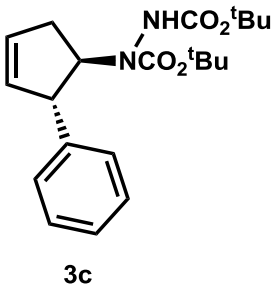
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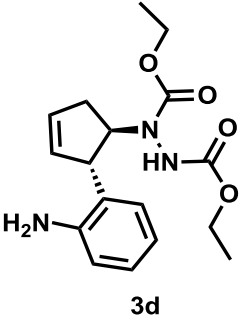
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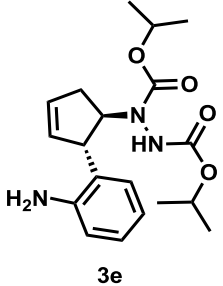
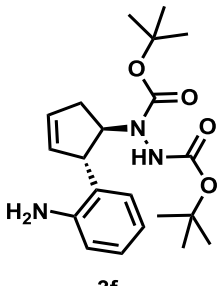
## Characterization of the Products

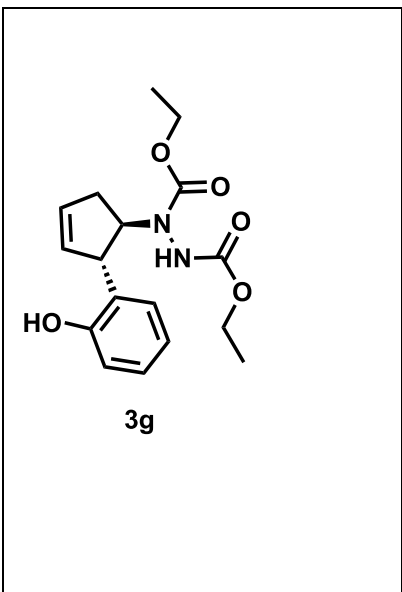
 <p style="text-align: center;"><b>3a</b></p>	<p><b>Diethyl 1-(2-phenylcyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3a</b></p> <p>Yield: 68 % as colourless viscous liquid; <math>R_f</math>: 0.53 (hexane/ethyl acetate = 6:4).</p> <p><b>IR</b> (Neat) <math>\nu_{\max}</math>: 3298, 3054, 2978, 2928, 2851, 1751, 1695, 1412, 1219, 1060, 943, 853, 757 <math>\text{cm}^{-1}</math>.</p> <p><b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.47-7.03 (m, 5H), 6.67 (s, 1H), 5.87-5.85 (m, 1H), 5.72-5.70 (m, 1H), 4.77-4.74 (m, 1H), 4.25-4.18 (m, 2H), 4.00 (s, 3H), 2.73-2.59 (m, 2H), 1.31-1.04 (m, 6H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 157.0, 156.0, 143.3, 132.7, 129.8, 129.7, 128.8, 128.4, 127.5, 126.5, 67.3, 62.4, 62.1, 53.8, 35.1, 14.5, 14.2. <b>MS (EI)</b>: Calcd for <math>\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_4</math>, (<math>\text{M}^+</math>): 318.1580; Found: 318.1577.</p>
 <p style="text-align: center;"><b>3b</b></p>	<p><b>Diisopropyl 1-(2-Phenylcyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3b</b></p> <p>Yield: 65 % as colourless viscous liquid; <math>R_f</math>: 0.46 (hexane/ethyl acetate = 6:4). <b>IR</b> (Neat) <math>\nu_{\max}</math>: 3291, 3054, 2981, 2928, 2862, 1742, 1698, 1492, 1386, 1260, 1176, 1108, 1034, 954, 757, 700 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.28-7.20 (m, 5H), 6.51 (s, 1H), 5.88-5.80 (m, 1H), 5.72-5.69 (m, 1H), 5.03-4.95 (m, 1H), 4.92-4.70 (m, 2H), 3.99 (s, 1H), 2.64-2.60 (m, 2H), 1.29-1.13 (m, 12 H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.3, 155.0, 143.5, 132.1, 129.9, 128.1, 127.9, 126.8, 70.4, 70.0, 69.6, 53.0, 35.0, 22.0, 21.8. <b>MS (EI)</b>: Calcd for <math>\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_4</math> (<math>\text{M}^+</math>): 347.1893; Found: 347.1895.</p>

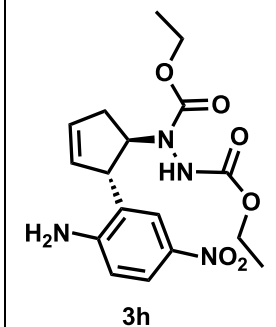
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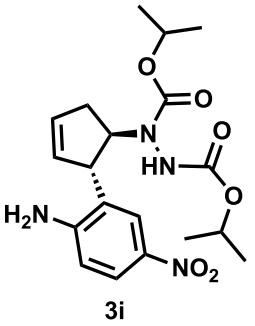
 <p>3c</p>	<p><b>Di-tert-butyl 1-(2-phenylcyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3c</b></p> <p>Yield: 60 % as colourless viscous liquid; <math>R_f</math>: 0.47 (hexane/ethyl acetate = 6:4). <b>IR</b> (Neat) <math>\nu_{\max}</math>: 3278, 3051, 2961, 2929, 2866, 1741, 1696, 1492, 1380, 1266, 1186, 1108, 1033, 964, 759 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.28-7.20 (m, 5H), 6.49 (s, 1H), 5.87-5.82 (m, 1H), 5.73-5.69 (m, 1H), 4.97 (s, 1H), 3.99 (s, 1H), 2.74-2.54 (m, 2H), 1.29-1.14 (s, 18 H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.6, 154.7, 143.1, 131.4, 130.7, 129.3, 128.8, 128.3, 81.2, 80.9, 55.9, 45.0, 35.7, 28.2. <b>MS (EI)</b>: Calcd for <math>\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_4</math> (<math>\text{M}^+</math>): 374.2206; Found: 374.2201.</p>
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 <p style="text-align: center;"><b>3d</b></p>	<p><b>Diethyl-1-(-2-(2-aminophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3d</b></p> <p><b>Yield:</b> 96% as pale yellow solid. <math>R_f</math>: 0.23 (hexane/ethyl acetate = 6:4). Mp: 123°C. <b>IR</b> (Neat) <math>\nu_{\max}</math>: 3363, 2959, 2919, 2846, 1738, 1714, 1604, 1462, 1259, 1023, 869, 798 <math>\text{cm}^{-1}</math>.</p> <p><b><math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 6.94-6.86 (m, 2H) 6.59-6.56 (m, 3H), 5.84 (s, 1H), 5.66 (s, 1H), 4.68-4.66 (m, 1H), 4.16-4.13 (m, 2H), 4.05-4.02 (m, 3H), 2.67 (m, 1H), 2.42-2.40 (m, 1H), 1.24-1.22 (m, 3H), 1.08-1.02 (m, 3H). <b><math>^{13}\text{C}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 155.8, 154.1, 132.7, 132.1, 132.0, 131.9, 128.5, 128.4, 127.4, 62.5, 62.3, 49.4, 36.1, 14.5. <b>MS (EI):</b> Calcd for <math>\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_4</math>, <math>M^+</math>: 333.1689; Found: 333.1680.</p>
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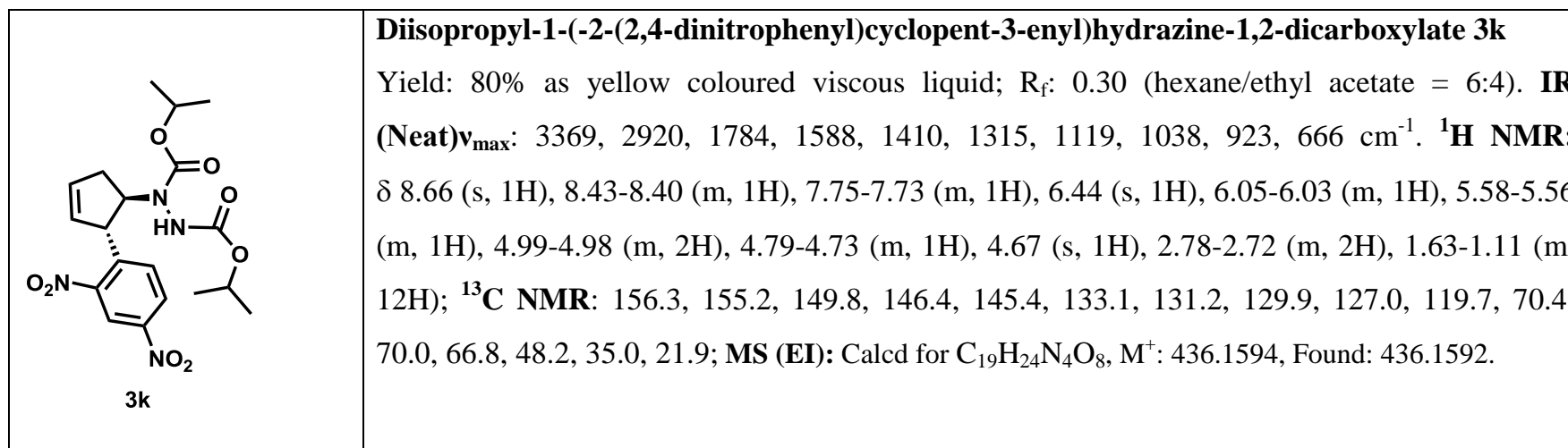
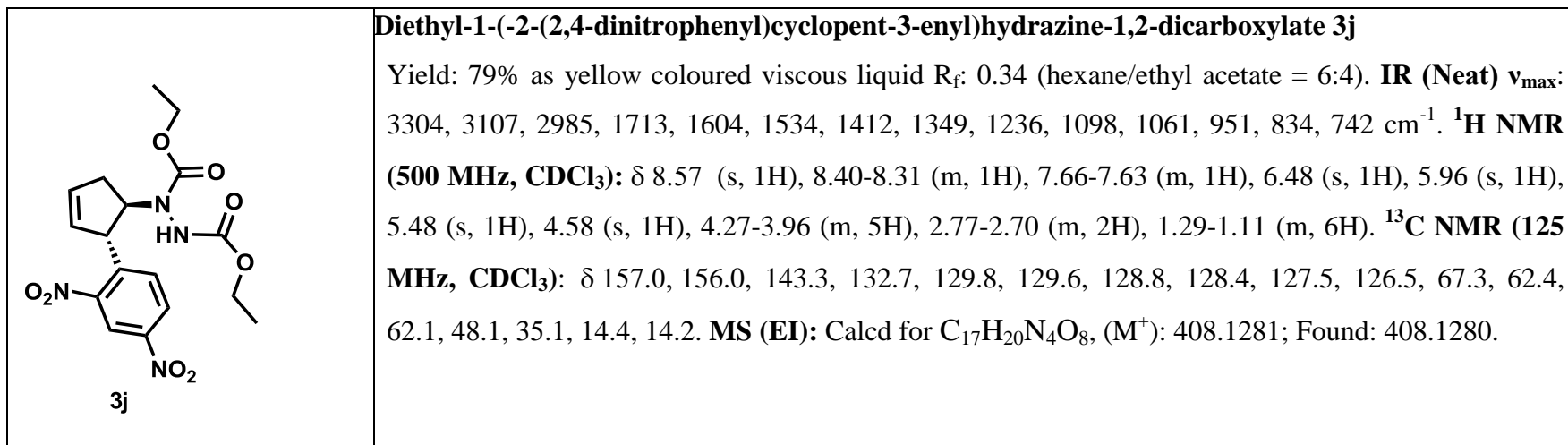
 <p style="text-align: center;"><b>3e</b></p>	<p><b>Diisopropyl-1-(2-(2-aminophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3e</b></p> <p>Yield: 92% as pale yellow solid. <math>R_f</math>: 0.46 (hexane/ethyl acetate = 6:4). mp: 126°C. <b>IR (KBr) <math>\nu_{\max}</math></b>: 3373, 3290, 3054, 2981, 1714, 1692, 1495, 1408, 1253, 1107, 1044, 953, 752 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H NMR}</math> (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 6.95-6.89 (m, 2H), 6.64 (brs, 2H), 6.47 (brs, 1H), 5.83 (s, 1H), 5.65 (s, 1H), 4.94-4.89 (m, 1H), 4.77 (brs, 1H), 4.67 (s, 1H), 4.04 (s, 1H), 2.63 (brs, 1H), 2.43 (brs, 1H), 1.22-1.09 (m, 12H). <b><math>^{13}\text{C NMR}</math> (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 157.2, 155.5, 144.1, 132.9, 130.1, 129.4, 128.7, 127.4, 118.8, 116.4, 70.3, 65.9, 64.2, 49.2, 35.9, 22.0, 21.9. <b>MS (EI)</b>: Calcd for <math>\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_4</math>, <math>M^+</math>: 361.2002; Found: 361.1998.</p>
 <p style="text-align: center;"><b>3f</b></p>	<p><b>Di-tert-butyl 1-(2-(2-aminophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3f</b></p> <p>Yield: 87% as colorless viscous liquid. <math>R_f</math>: 0.49 (hexane/ethyl acetate = 6:4). <b>IR (KBr) <math>\nu_{\max}</math></b>: 3364, 3060, 2978, 2928, 1709, 1692, 1495, 1393, 1252, 1158, 1020, 952, 751 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H NMR}</math> (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 6.93 (s, 1H), 6.88 (s, 1H), 6.61 (s, 2H), 6.21 (brs, 1H), 5.82 (s, 1H), 5.64 (s, 1H), 4.63 (s, 1H), 4.02 (s, 1H), 2.60 (brs, 1H), 2.48 (s, 1H), 1.42 (s, 18H). <b><math>^{13}\text{C NMR}</math> (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.1, 154.7, 147.3, 143.9, 133.0, 128.6, 127.3, 119.0, 116.5, 81.5, 63.9, 49.4, 35.8, 28.2, 28.1. <b>MS (EI)</b>: Calcd for <math>\text{C}_{21}\text{H}_{31}\text{N}_3\text{O}_4</math>, <math>M^+</math>: 389.2315; Found: 389.2332.</p>

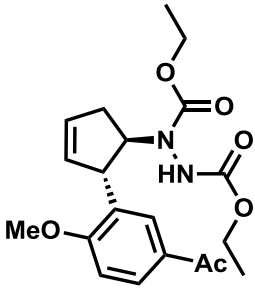
 <p style="text-align: center;"><b>3g</b></p>	<p style="text-align: center;"><b>Diethyl 1-(2-(2-hydroxyphenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3g</b></p> <p>Yield: 87% as colorless viscous liquid. <math>R_f</math>: 0.40 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{\max}</math>: 3443, 3290, 3051, 2959, 2919, 2846, 1744, 1719, 1600, 1454, 1235, 1155, 1049, 950, 751 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H NMR}</math> (300 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.31-7.17 (m, 5H), 6.37 (s, 1H), 5.87-5.85 (m, 1H), 5.72-5.69 (m, 1H), 4.75-4.72 (m, 1H), 4.26-4.19 (m, 2H), 4.00 (s, 3H), 2.68-2.58 (m, 2H), 1.33-1.25 (m, 3H), 1.06 (s, 3H). <b><math>^{13}\text{C NMR}</math> (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.7, 155.9, 143.2, 132.7, 129.6, 128.4, 127.4, 126.5, 67.2, 62.2, 62.1, 53.8, 35.1, 14.4, 14.2. <b>MS (EI)</b>: Calcd for <math>\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5</math>, (<math>\text{M}^+</math>): 334.1529; Found: 334.1536.</p>
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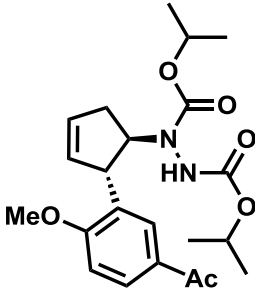
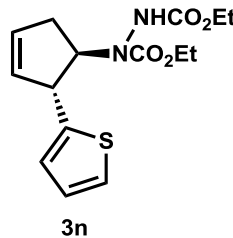
 <p style="text-align: center;"><b>3h</b></p>	<p><b>Diethyl 1-(-2-(2-amino-5-nitrophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3h</b></p> <p>Yield: 88% as colorless viscous liquid. <math>R_f</math>: 0.42 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{\max}</math>: 3346, 3065, 2980, 2932, 1713, 1693, 1607, 1494, 1258, 1162, 1063, 955, 753 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.86-7.84 (m, 1H), 7.76 (s, 1H), 6.66 (brs, 1H) 6.47-6.46 (d, 1H, <math>J = 8.5</math> Hz), 5.94 (s, 1H), 5.64 (s, 1H), 5.46 (brs, 2H), 4.64-4.63 (m, 1H), 4.14-4.13 (m, 3H), 4.01-3.99 (m, 2H), 2.77 (brs, 1H), 2.49 (brs, 1H), 1.23 (m, 6H). <b><math>^{13}\text{C}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.6, 155.6, 151.9, 138.4, 132.2, 131.9, 128.5, 124.5, 113.7, 62.7, 62.1, 49.0, 36.1, 14.4. <b>MS (EI)</b>: Calcd for <math>\text{C}_{17}\text{H}_{22}\text{N}_4\text{O}_6</math>, (<math>\text{M}^+</math>): 378.1539; Found: 378.1555.</p>
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 <p style="text-align: center;"><b>3i</b></p>	<p><b>Diisopropyl 1-(2-(2-amino-5-nitrophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3i</b></p> <p>Yield: 89% as colorless viscous liquid. <math>R_f</math>: 0.58 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{\max}</math>: 3330, 3051, 2976, 2927, 1715, 1700, 1615, 1472, 1329, 1255, 1155, 958, 751 <math>\text{cm}^{-1}</math>.</p> <p><b><math>^1\text{H NMR}</math> (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.88-7.86 (m, 1H), 7.80 (s, 1H), 6.49 (s, 1H), 6.40-6.30 (m, 1H), 5.93 (s, 1H), 5.61 (s, 1H), 4.94-4.88 (m, 1H), 4.78 (s, 1H), 4.66 (s, 1H), 4.06-4.03 (m, 1H), 2.50-2.48 (m, 1H), 2.33-2.31 (m, 1H), 1.26-1.22 (m, 12H). <b><math>^{13}\text{C NMR}</math> (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.2, 155.0, 151.8, 138.4, 131.4, 131.0, 126.3, 124.5, 124.1, 113.8, 70.7, 69.9, 63.3, 49.0, 36.1, 22.0, 21.9. <b>MS (EI)</b>: Calcd for <math>\text{C}_{19}\text{H}_{26}\text{N}_4\text{O}_6</math>, <math>M^+</math>: 406.1852; Found: 406.1840.</p>
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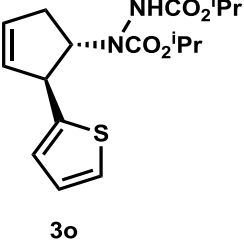


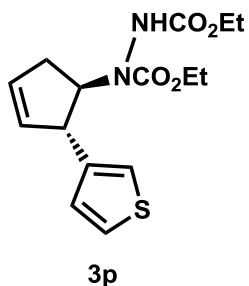


 <p style="text-align: center;"><b>31</b></p>	<p><b>Diethyl 1-(2-(5-acetyl-2-methoxyphenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 31</b> Yield: 83% as colorless viscous liquid. <math>R_f</math> : 0.30 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{\max}</math>: 3373, 3054, 2981, 2935, 1714, 1692, 1635, 1495, 1408, 1253, 1107, 953, 752 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.87-7.85 (m, 1H), 7.81-7.80 (m, 1H), 6.88-6.86 (m, 1H), 6.53 (s, 1H), 5.93-5.92 (m, 1H), 5.68-5.67 (m, 1H), 4.70 (brs, 1H), 4.39-4.38 (m, 1H), 4.24-4.22 (m, 2H), 4.01-3.92 (m, 2H), 3.89 (s, 3H), 2.71-2.68 (m, 1H), 2.55-2.52 (m, 1H), 2.47 (s, 3H), 1.32-1.31 (m, 6H). <b><math>^{13}\text{C}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 196.5, 160.9, 157.2, 156.1, 131.2, 129.0, 128.1, 109.5, 62.2, 62.0, 55.9, 45.2, 35.2, 26.3, 14.5. <b>MS (EI)</b>: Calcd for <math>\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_6</math>, <math>\text{M}^+</math>: 390.1791, Found: 390.1780.</p>
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 <p style="text-align: center;"><b>3m</b></p>	<p><b>Diisopropyl 1-(2-(5-acetyl-2-methoxyphenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3m</b></p> <p>Yield: 84% as colorless viscous liquid. <math>R_f</math>: 0.34 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{\max}</math>: 3285, 3054, 2978, 2917, 1709, 1684, 1596, 1360, 1256, 1108, 1020, 957, 735 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.85-7.83 (m, 1H), 7.79-7.78 (m, 1H), 6.86-6.84 (d, 1H, <math>J = 9.0</math> Hz), 6.38 (s, 1H), 5.93-5.92 (m, 1H), 5.67 (s, 1H), 4.99-4.98 (m, 1H), 4.66 (brs, 2H), 4.37 (s, 1H), 3.89 (s, 3H), 2.70 (s, 1H), 2.59 (s, 1H), 2.55 (s, 3H), 1.31 (m, 12H). <b><math>^{13}\text{C}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 195.9, 168.0, 156.8, 155.8, 131.2, 128.9, 128.2, 119.2, 109.6, 69.7, 55.9, 45.5, 35.3, 26.3, 21.9. <b>MS (EI)</b>: Calcd for <math>\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_6</math>, <math>M^+</math>: 418.2104; Found: 418.2120.</p>
 <p style="text-align: center;"><b>3n</b></p>	<p><b>Diethyl 1-(2-(thiophen-2-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3n</b></p> <p>Yield: 67 % as colourless viscous liquid; <math>R_f</math>: 0.38 (hexane/ethyl acetate = 6:4). <b>IR (Neat)</b> <math>\nu_{\max}</math>: 3295, 3060, 2980, 2935, 2866, 1750, 1680, 1515, 1475, 1412, 1126, 1057, 948, 759, 691 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 7.19-7.01 (m, 1H), 6.91-6.71 (m, 2H), 6.43 (s, 1H), 5.84-5.65 (m, 2H), 4.79 (s, 1H), 4.31-4.07 (m, 5H), 2.59-2.46 (m, 2H), 1.47-1.19 (m, 6H). <b><math>^{13}\text{C}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>)</b>: <math>\delta</math> 156.6, 155.5, 132.5, 129.3, 126.7, 123.5, 120.4, 63.4, 62.1, 61.9,</p>

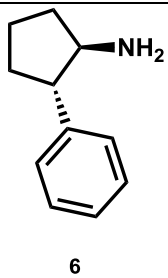
	49.5, 35.9, 14.9, 14.4. <b>MS (EI)</b> : Calcd for C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> S (M <sup>+</sup> ): 324.1144; Found: 324.111.
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 <p>30</p>	<p><b>Diisopropyl 1-(2-(2-thiophen-2-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate</b> <b>30</b></p> <p>Yield: 53 % as colourless viscous liquid; R<sub>f</sub>: 0.39 (hexane/ethyl acetate = 6:4). <b>IR</b> (Neat) ν<sub>max</sub>: 3330, 3051, 2976, 2927, 1715, 1700, 1615, 1472, 1329, 1255, 1155, 958, 751 cm<sup>-1</sup>. <b><sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)</b>: δ 7.15–7.11 (m, 1H), 6.94–6.86 (m, 2H), 6.30 (s, 1H), 5.95–5.79 (m, 2H), 5.11–4.95 (m, 2H), 4.69 (s, 1H), 4.11 (s, 1H), 2.87–2.45 (m, 2H), 1.35–1.09 (m, 12H). <b><sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)</b>: δ 156.7, 155.4, 129.9, 127.3, 126.7, 123.4, 120.4, 69.9, 63.9, 53.9, 35.9, 22.1, 22.0 <b>MS (EI)</b>: Calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>S (M<sup>+</sup>): 352.1457; Found: 352.1462.</p>
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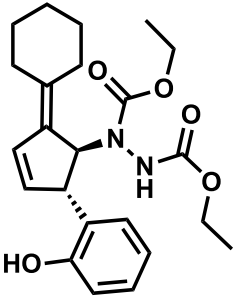
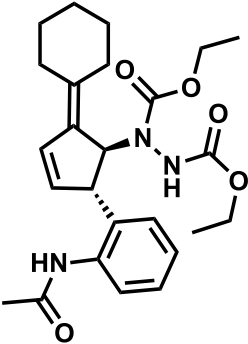
**Diethyl 1-(2-(thiophen-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 3p**

Yield: 71 % as colourless viscous liquid;  $R_f$ : 0.43 (hexane/ethyl acetate = 6:4). **IR** (Neat)  $\nu_{\max}$ : 3330, 3051, 2976, 2927, 1715, 1700, 1615, 1472, 1329, 1255, 1155, 958, 751  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**:  $\delta$  7.29–7.06 (m, 1H), 6.98–6.76 (m, 2H), 6.40 (s, 1H), 5.84–5.79 (m, 2H), 4.80 (s, 1H), 4.26–4.12 (m, 5H), 2.66–2.60 (m, 2H), 1.33–1.18 (m, 6H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**:  $\delta$  156.9, 156.7, 132.5, 129.3, 127.1, 125.5, 120.3, 64.0, 62.4, 62.1, 49.0, 35.0, 14.5, 14.4. **MS (EI)**: Calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$  ( $\text{M}^+$ ): 324.1144; Found: 324.1141.

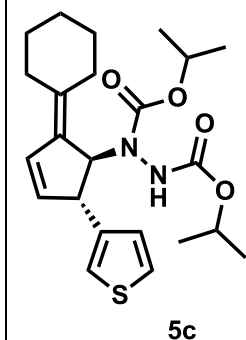


***trans*-2-phenylcyclopentylamine 6**

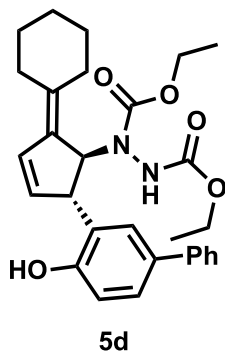
Yield: 40 % as colourless viscous liquid;  $R_f$ : 0.39 (hexane/ethyl acetate = 6:4).  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**: 7.35–7.19 (m, 5 H), 4.73–4.54 (m, 1 H), 3.38–3.10 (m, 1H), 2.20–1.58 (m, 6 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**:  $\delta$  143.6, 128.5, 127.4, 127.3, 126.4, 126.2, 54.5, 49.9, 33.2, 31.1, 24.0. Mass Spectrometric Analysis: **MS (EI)** for  $\text{C}_{11}\text{H}_{15}\text{N}$ , Calcd ( $\text{M}^+$ ): 161.1204, Found ( $\text{M}^+$ ): 161.1201.

 <p>5a</p>	<p><b>Diethyl 1-(2-cyclohexylidene-5-(2-hydroxyphenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 5a.</b> Yield: 90% as colorless viscous liquid. <math>R_f</math>: 0.52 (hexane/ethyl acetate = 6:4). <b>IR (KBr) <math>\nu_{max}</math>:</b> 3452, 3286, 2934, 2844, 1740, 1720, 1465, 1410, 1366, 1130, 1055, 920, 751, 700 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 7.83 (s, 1H), 7.15-7.10 (m, 1H), 6.94-6.81 (m, 3H), 6.67-6.48 (m, 1H), 6.35-6.25 (m, 1H), 5.91 (m, 1H), 5.09 (m, 1H), 4.41-4.32 (m, 5H), 2.34 (m, 2H), 2.03 (m, 2H), 1.67-1.56 (m, 4H), 1.43 (m, 1H), 1.29-1.27 (m, 5H), 1.12-1.10 (m, 2H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 156.2, 156.0, 141.0, 139.4, 135.4, 129.9, 129.7, 128.3, 123.0, 113.1, 62.4, 61.3, 60.4, 50.3, 31.9, 31.4, 27.8, 27.3, 26.5, 14.9, 14.6. <b>MS (FAB):</b> Calcd for <math>\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_5</math>, (<math>\text{M}^+</math>): 414.22; Found: 414.15.</p>
 <p>5b</p>	<p><b>Diethyl 1-(2-(2-acetamidophenyl)-5-cyclohexylidene-cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 5b.</b> Yield: 96% as colorless viscous liquid. <math>R_f</math>: 0.44 (hexane/ethyl acetate = 6:4). <b>IR (KBr) <math>\nu_{max}</math>:</b> 3433, 3206, 2928, 2824, 1750, 1717, 1524, 1320, 1252, 1065, 928, 821 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 8.69-8.60 (m, 2H), 7.24-7.22 (m, 1H), 7.00-6.95 (m, 2H), 6.62 (m, 1H), 6.47-6.36 (m, 1H), 5.88 (m, 1H), 5.00-4.95 (m, 1H), 4.33-4.09 (m, 5H), 2.33 (m, 2H), 2.20 (s, 3H), 2.03-1.99 (m, 2H), 1.89 (s, 2H), 1.29-1.24 (m, 4H), 1.12-1.07 (m, 6H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 169.8, 156.7, 156.0, 136.4, 135.8, 133.8, 131.5, 127.6, 127.2, 125.8, 124.9, 123.9, 110.9, 62.8, 62.4, 61.9, 49.5, 30.4, 28.2, 26.4, 25.6, 24.8, 23.9, 14.4. <b>MS (FAB):</b> Calcd for <math>\text{C}_{25}\text{H}_{33}\text{N}_3\text{O}_5</math>, (<math>\text{M}^+</math>): 455.24;</p>

Found: 455.19.

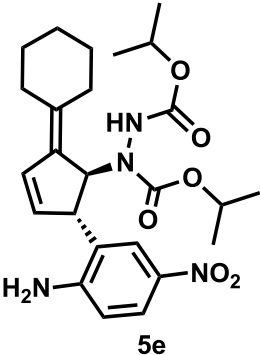
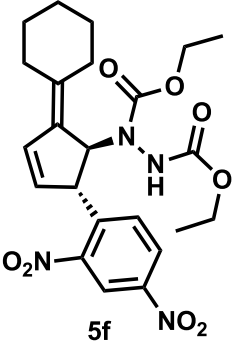


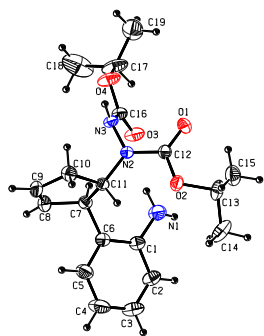
**Diisopropyl 1-(2-cyclohexylidene-5-(thiophen-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 5c.** Yield: 64% as colorless viscous liquid.  $R_f$ : 0.64 (hexane/ethyl acetate = 6:4). **IR (KBr)  $\nu_{max}$ :** 3366, 2980, 1748, 1716, 1676, 1577, 1444, 1386, 1223, 1105, 1065, 754, 702  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.86 (s, 1H), 7.01 (s, 1H), 6.65-6.47 (m, 2H), 6.16 (s, 1H), 5.92-5.78 (m, 1H), 4.90 (m, 3H), 4.46-4.37 (m, 1H), 2.43-2.03 (m, 4H), 1.63-1.55 (m, 4H), 1.45-1.40 (m, 2H), 1.28-1.22 (m, 12H).  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):**  $\delta$  156.0, 155.1, 140.1, 134.7, 128.8, 127.3, 127.0, 126.8, 123.7, 71.7, 70.8, 62.0, 48.0, 32.0, 29.7, 28.0, 27.1, 26.0, 22.0. **MS (FAB):** Calcd for  $\text{C}_{23}\text{H}_{32}\text{N}_2\text{O}_4\text{S}$ , ( $\text{M}^+$ ): 432.21; Found: 432.19.



**Diethyl 1-(-2-cyclohexylidene-5-(4-hydroxybiphenyl-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 5d.** Yield: 91% as colorless viscous liquid.  $R_f$ : 0.54 (hexane/ethyl acetate = 6:4). **IR (KBr)  $\nu_{max}$ :** 3457, 3204, 2934, 2818, 1736, 1717, 1501, 1432, 1233, 1078, 867, 752  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.99 (s, 1H), 7.59 (m, 3H), 7.51-7.39 (m, 1H), 7.35-7.30 (m, 1H), 7.06-6.89 (m, 2H), 6.76-6.71 (m, 1H), 5.99 (s, 1H), 5.81-5.79 (m, 1H), 5.53-5.52 (m, 1H), 4.24-4.03 (m, 5H), 2.65-2.51 (m, 2H), 2.17-2.11 (m, 2H), 1.57-1.42 (m, 6H), 1.25-1.22 (m, 6H).  **$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):**  $\delta$  156.3, 155.5, 139.2, 137.9, 135.5, 128.9, 128.2, 127.3, 126.8, 112.8, 107.3, 65.8, 62.5, 61.3, 57.4, 32.0, 31.5, 27.8, 27.3, 26.5, 14.6. **MS (FAB):** Calcd for  $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_5$ , ( $\text{M}^+$ ): 490.25; Found: 490.28.



 <p style="text-align: center;"><b>5e</b></p>	<p><b>Diisopropyl 1-(2-(2-amino-5-nitrophenyl)-5-cyclohexylidene)cyclopent-3-enylhydrazine-1,2-dicarboxylate 5e</b> Yield: 83% as colorless viscous liquid. <math>R_f</math>: 0.60 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{max}</math>: 3350, 3052, 2965, 2934, 1730, 1698, 1607, 1500, 1254, 1202, 1055, 978, 753 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 8.59 (s, 1H), 8.21-8.18 (m, 1H), 7.29 (s, 1H), 7.10-7.07 (m, 1H), 6.76-6.75 (m, 1H), 6.19-6.13 (m, 1H), 5.94 (s, 1H), 5.77 (s, 1H), 5.11-4.89 (m, 3H), 4.19 (s, 1H), 2.36 (s, 2H), 2.09 (s, 2H), 1.64 (m, 6H), 1.33-1.28 (m, 12H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>):</b> 157.0, 156.8, 150.9, 138.7, 135.0, 132.1, 126.2, 112.2, 106.7, 70.5, 70.1, 63.2, 50.1, 31.4, 31.1, 29.7, 28.3, 26.3, 22.03. <b>MS (FAB):</b> Calcd for <math>\text{C}_{25}\text{H}_{34}\text{N}_4\text{O}_6</math>, (<math>\text{M}^+</math>): 486.25; Found: 486.20.</p>
 <p style="text-align: center;"><b>5f</b></p>	<p><b>Diethyl 1-(2-(2-cyclohexylidene-5-(2,4-dinitrophenyl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate 5f.</b> Yield: 81% as colorless viscous liquid. <math>R_f</math>: 0.50 (hexane/ethyl acetate = 6:4). <b>IR (KBr)</b> <math>\nu_{max}</math>: 3330, 3118, 2967, 1724, 1704, 1523, 1412, 1320, 1236, 1056, 1079, 947, 754 <math>\text{cm}^{-1}</math>. <b><math>^1\text{H}</math> NMR (300 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 8.76 (s, 1H), 8.35 (d, <math>J = 8.10</math> Hz, 1H), 7.60 (s, 1H), 6.92 (s, 1H), 6.59-6.40 (m, 1H), 5.77 (s, 1H), 5.70 (brs, 1H), 4.15-4.00 (m, 5H), 2.34-2.20 (m, 4H), 1.61-1.59 (m, 6H), 1.32-1.24 (m, 6H). <b><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{CDCl}_3</math>):</b> <math>\delta</math> 156.6, 156.0, 155.4, 149.0, 139.4, 135.3, 129.6, 128.2, 123.0, 116.0, 62.6, 61.6, 61.4, 48.4, 31.9, 31.4, 27.7, 27.2, 26.4, 14.5, 14.3. <b>MS (FAB):</b> Calcd for <math>\text{C}_{23}\text{H}_{28}\text{N}_4\text{O}_8</math>, (<math>\text{M}^+</math>): 488.19; Found: 488.28.</p>



ORTEP drawing: **3e**

Empirical formula	$C_{19}H_{27}N_3O_4$
Formula weight	361.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	TRICLINIC
Space group	P-1
Unit cell dimensions	a = 9.524(3) Å    alpha = 96.259(5) deg. b = 9.968(3) Å    beta = 102.562(5) deg. c = 10.582(3) Å    gamma = 90.735(5) deg.
Volume	973.9(5) Å <sup>3</sup>
Z	2

Density (calculated)	1.232 Mg/m <sup>3</sup>
Absorption coefficient	0.087 mm <sup>-1</sup>
F(000)	388
Crystal size	0.32 x 0.24 x 0.16 mm
Theta range for data collection	1.98 to 26.00 deg.
Index ranges	-11<=h<=11, -12<=k<=12, -13<=l<=13
Reflections collected	7494
Independent reflections	3770 [R(int) = 0.0232]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9862 and 0.9727
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3770 / 0 / 247
Goodness-of-fit on F <sup>2</sup>	1.182
Final R indices [I>2sigma(I)]	R1 = 0.0783, wR2 = 0.1668
R indices (all data)	R1 = 0.0925, wR2 = 0.1750
Largest diff. peak and hole	0.227 and -0.187 e.A <sup>-3</sup>

