

Supporting information for

Title: New approach to the synthesis of azinylcymantrenes

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Table S1. R_f, IR, Elemental Analysis, and HRMS Data for **4a-j**, **3j** and **5**.

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Table S1. R_f, IR, Elemental Analysis, and ESI-MS Data for **4a-j**, **3j** and **5**.

	R_f (eluent)	IR (cm⁻¹)	Elemental analysis	ESI-MS
4a	0.5 (benzene:EtOAc, 9.5:0.5)	$\nu(\text{CO})$ 2010, 1917	Found: C, 55.27; H, 3.31; N, 4.66 Calc for C ₁₃ H ₈ MnNO ₃ : C, 55.52; H, 2.85; N, 4.98	282
4b	0.2 (hexane:EtOAc, 8:2)	$\nu(\text{CO})$ 2001, 1922, 1908	Found: C, 59.65; H, 3.11; N, 7.51 Calc for C ₁₈ H ₁₁ MnN ₂ O ₃ : C, 60.34; H, 3.07; N, 7.82	359
4c	0.5 (CH ₂ Cl ₂)	$\nu(\text{CO})$ 2011, 1940, 1911	Found: C, 61.35; H, 3.18; N, 4.12 Calc for C ₁₇ H ₁₀ MnNO ₃ : C, 61.63; H, 3.02; N, 4.23	332
4d	0.4 (CH ₂ Cl ₂)	$\nu(\text{CO})$ 2011, 1910	Found: C, 61.60; H, 2.88; N, 4.17 Calc for C ₁₇ H ₁₀ MnNO ₃ : C, 61.63; H, 3.02; N, 4.23	332
4e	0.3 (benzene:EtOAc, 9.5:0.5)	$\nu(\text{CO})$ 2021, 2012, 1923	Found: C, 66.12; H, 3.09; N, 3.59 Calc for C ₂₁ H ₁₂ MnNO ₃ : C, 66.14; H, 3.15; N, 3.67	382
4f	0.3 (EtOAc)	$\nu(\text{CO})$ 2021, 2012, 1929, 1915	Found: C, 50.95; H, 2.63; N, 9.55 Calc for C ₁₂ H ₇ MnN ₂ O ₃ : C, 51.06; H, 2.48; N, 9.93	283
4g	0.6 (EtOAc)	$\nu(\text{CO})$ 2014, 1913	Found: C, 51.03; H, 2.27; N, 9.93 Calc for C ₁₂ H ₇ MnN ₂ O ₃ : C, 51.06; H, 2.48; N, 9.93	283
4h	0.4 (CH ₂ Cl ₂)	$\nu(\text{CO})$ 2016, 1947, 1917	Found: C, 56.34; H, 3.31; N, 8.57 Calc for C ₁₆ H ₉ MnN ₂ O ₃ : C, 57.83; H, 2.71; N, 8.43	333
4i	0.4 (hexane:EtOAc, 1:1)	$\nu(\text{CO})$ 2012, 1910	Found: C, 62.74; H, 2.95; N, 7.13 Calc for C ₂₀ H ₁₁ MnN ₂ O ₃ : C, 62.83; H, 2.88; N, 7.33	383
4j	0.5 (benzene:EtOAc, 9.5:0.5)	$\nu(\text{CO})$ 2016, 1914	Found: C, 63.49; H, 3.54; N, 9.66 Calc for C ₂₃ H ₁₄ MnN ₃ O ₃ : C, 63.45; H, 3.22; N, 9.66	436

3j	0.2 (benzene)	$\nu(\text{NH})$ 2954, 2923, 2853, $\nu(\text{CO})$ 2012, 1915	Found: C, 63.63; H, 3.38; N, 9.34 Calc for $\text{C}_{23}\text{H}_{16}\text{MnN}_3\text{O}_3$: C, 63.16; H, 3.66; N, 9.61	438
5	0.2 (benzene:EtOAc, 9:1)	$\nu(\text{CO})$ 2015, 1948, 1921	Found: C, 64.24; H, 4.56; N, 8.60 Calc for $\text{C}_{25}\text{H}_{20}\text{MnN}_3\text{O}_3$: C, 64.52; H, 4.30; N, 9.03	466

Table S2. ^1H and ^{13}C NMR data for products.

Compound	^1H NMR data	^{13}C NMR data
4a	4.99 (m, 2H, C ₅ H ₄), 5.76 (m, 2H, C ₅ H ₄), 7.20 (s, 1H, 5'-H), 7.66 (m, 2H, 3'-H, 4'-H), 8.48 (s, 1H, 2'-H)	82.38, 82.61 (CH-Cp); 100.24 (C-Cp); 119.67 (C3); 122.57 (C5); 136.52 (C4); 149.48 (C6); 152.16 (C2)
4b	4.85 (m, 2H, C ₅ H ₄), 5.63 (m, 2H, C ₅ H ₄), 7.31 (m, 1H, 5'-H), 7.35 (d, 1H, $^3J = 7.8$ Hz, 5-H), 7.77 (t, 1H, $^3J = 7.8$ Hz, 4-H), 7.83 (t, 1H, $^3J = 7.8$ Hz, 4'-H), 8.29 (d, 1H, $^3J = 7.5$ Hz, 3-H), 8.49 (d, 1H, $^3J = 8.0$ Hz, 3'-H), 8.66 (d, 1H, $^3J = 4.3$ Hz, 6'-H)	82.43, 83.13 (CH-Cp); 100.24 (C-Cp); 119.52 (C5); 119.83 (C3); 121.32 (C3'); 123.89 (C5'); 136.93 (C4'); 137.57 (C4); 149.07 (C6'); 151.55 (C6); 155.82 (C2'); 155.88 (C2)
4c	4.92 (m, 2H, C ₅ H ₄), 5.73 (m, 2H, C ₅ H ₄), 7.46 (d, 1H, $^3J = 8.5$ Hz, 4-H), 7.54 (m, 1H, 7-H), 7.73 (m, 1H, 6-H), 7.80 (d, 1H, $^3J = 8.3$ Hz, 5-H), 8.06 (d, 1H, $^3J = 8.6$ Hz, 8-H), 8.15 (d, 1H, $^3J = 8.5$ Hz, 3-H)	82.85, 83.44 (CH-Cp); 100.12 (C-Cp); 118.06 (C4); 126.53 (C7); 127.36 (C8a); 127.57 (C5); 129.39 (C8); 129.91 (C6); 136.66 (C3); 147.99 (C4a); 152.27 (C2)
4d	4.93 (m, 2H, C ₅ H ₄), 5.30 (m, 2H, C ₅ H ₄), 7.59 (d, 1H, $^3J = 5.6$ Hz, 5-H), 7.79 (m, 1H, 6-H), 8.25 (m, 1H, 7-H), 7.86 (d, 1H, $^3J = 8.4$ Hz, 8-H), 8.38 (d, 1H, $^3J = 8.6$ Hz, 4-H), 8.51 (d, 1H, $^3J = 5.6$ Hz, 3-H)	82.36, 85.58 (CH-Cp); 103.05 (C-Cp); 120.69 (C5); 125.60 (C4); 126.25 (C8a); 127.49 (C6); 127.62 (C8); 130.00 (C7); 136.75 (C4a); 141.98 (C3); 152.29 (C1)
4e	5.09 (m, 2H, C ₅ H ₄), 5.50 (m, 2H, C ₅ H ₄), 7.61 (m, 2H, 2-H, 7-H), 7.80 (m, 2H, 3-H, 6-H), 8.16 (d, 2H, $^3J = 7.0$ Hz, 1-H, 8-H), 8.59 (d, 2H, $^3J = 8.04$ Hz, 4-H, 5-H)	82.46, 87.66 (CH-Cp); 99.72 (C-Cp); 125.05 (C8a, C10a); 125.72 (C4, C5); 126.09 (C2, C7); 129.93 (C3, C6); 130.59 (C1, C8); 136.26 (C4a, C9a); 148.76 (C9)
4f	4.98 (m, 2H, C ₅ H ₄), 5.43 (m, 2H, C ₅ H ₄), 7.42 (s, 1H, 4-H), 9.17 (s, 1H, 6-H), 9.24 (s, 1H, 5-H)	82.80, 83.52 (CH-Cp); 92.79 (C-Cp); 121.72 (C4); 133.05 (C3); 148.46 (C5); 151.27 (C6)
4g	4.92 (m, 2H, C ₅ H ₄), 5.66 (m, 2H, C ₅ H ₄), 7.30 (s, 1H, 5-H), 8.71 (d, 1H, $^3J = 2.5$ Hz, 6-H), 9.15 (s, 1H, 2-H)	83.26, 84.20 (CH-Cp); 94.80 (C-Cp); 116.19 (C5); 157.35 (C6); 159.18 (C2); 160.67 (C4)
4h	5.15 (m, 2H, C ₅ H ₄), 6.13 (m, 2H, C ₅ H ₄), 7.77 (m, 2H, 6-H, 7-H), 8.00 (m, 2H, 5-H, 8-H), 9.20 (s, 1H, 3-H)	83.30, 83.92 (CH-Cp); 96.07 (C-Cp); 129.35 (C8); 129.41 (C5); 129.86 (C6); 130.71 (C7); 141.80 (C4a); 142.22 (C8a); 142.28 (C3); 147.97 (C2)
4i	4.93 (m, 2H, C ₅ H ₄), 5.83 (m, 2H, C ₅ H ₄), 7.62 (m, 1H, 8-H), 7.68 (d, 1H, $^3J = 8.6$ Hz, 3-H), 7.77 (m, 2H, 5-H, 6-H), 8.23 (t, 2H, $^3J = 8.2$ Hz, 7-H, 4-H), 9.21 (d, 1H, $^3J = 3.2$ Hz, 9-H)	82.19, 83.65 (CH-Cp); 101.50 (C-Cp); 120.54 (C3); 123.16 (C8); 126.46 (C6); 126.77 (C5); 127.99 (C4a); 129.30 (C6a); 136.25 (C7); 136.86 (C4); 145.95 (C1a); 146.12 (C10a); 150.57 (C9); 152.84 (C2)
4j	4.82 (m, 2H, C ₅ H ₄), 5.30 (m, 2H, C ₅ H ₄), 7.61 (m, 6H, Ph), 7.67 (m, 2H, Ph), 8.65 (m, 2H, Ph)	82.88, 88.05 (CH-Cp); 91.98 (C-Cp); 128.37, 128.86, 129.05, 129.13, 129.95, 131.72 (CH-Ph); 134.51, 135.35 (C-Ph); 151.18 (C6); 154.40 (C5); 161.41 (C3)

3j	4.47 (s, 1H, C ₅ H ₄), 4.54 (s, 1H, C ₅ H ₄), 4.82 (s, 1H, C ₅ H ₄), 4.89 (s, 1H, C ₅ H ₄), 5.77 (s, 1H, 5-H), 7.49 (m, 6H, Ph), 7.82 (m, 4H, Ph), 8.98 (s, 1H, NH)	49.79 (C5); 79.51, 81.18, 84.41, 85.03 (CH-Cp); 100.85 (C-Cp); 126.24, 126.56, 128.87, 128.94, 129.90, 131.30 (CH-Ph); 132.20, 134.04 (C-Ph); 143.56 (C6); 153.12 (C3)
5	1.03 (t, 3H, ³ J = 6.7 Hz, N-CH ₂ -Me), 3.51 (m, 2H, N-CH ₂ -Me), 4.61 (d, 1H, ³ J = 1.5 Hz, C ₅ H ₄), 4.75 (m, 2H, C ₅ H ₄), 5.24 (t, 1H, ³ J = 1.5 Hz, C ₅ H ₄), 5.60 (s, 1H, 5-H), 7.48 (m, 6H, Ph), 7.80 (t, 2H, ³ J = 6.2 Hz, Ph), 8.17 (t, 2H, ³ J = 1.5 Hz, Ph)	15.18 (N-CH ₂ -Me); 45.63 (N-CH ₂ -Me); 45.68 (C5); 80.21, 81.13, 84.87, 85.16 (CH-Cp); 97.46 (C-Cp); 126.35, 127.80, 128.09, 128.79, 129.29, 130.17 (CH-Ph); 132.81, 133.41 (C-Ph); 148.06 (C6); 151.69 (C3)

Table S3. Crystal and refinement data for **4h** and **5**.

Identification code	4h	5
Formula	C ₁₆ H ₉ MnN ₂ O ₃	C ₂₅ H ₂₀ MnN ₃ O ₃
Molecular weight	332.19	465.38
T/K	295(2)	120(2)
$\lambda/\text{\AA}$	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> / \AA	10.1631(14)	17.2740(13)
<i>b</i> / \AA	12.7084(16)	10.3238(8)
<i>c</i> / \AA	11.9261(19)	12.4326(6)
β /deg	114.609(15)	101.833(5)
<i>V</i> / \AA^3	1400.4(3)	2170.0(3)
<i>Z</i>	4	4
<i>d</i> _{calc} /g cm ⁻³	1.576	1.424
μ /mm ⁻¹	0.956	0.641
<i>F</i> (000)	672	960
Crystal dimensions/mm	0.24 x 0.13 x 0.07	0.26 x 0.13 x 0.07
2 θ -Scan range/deg	2.74 – 28.28	2.71 – 30.54
Completeness based on 2 θ _{max} , %	96.4	97.4
hkl ranges	-12 < h < 13 -16 < k < 5 -15 < l < 6	-22 < h < 24 -14 < k < 12 -10 < l < 17
Total number of reflections	4351	13685
Number of independent reflections	3348	6475
<i>R</i> _{int}	0.0167	0.0259
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	2315	4320
Number of refined parameters	199	289
Absorption correction	analytical	analytical

Transmission (maximum/minimum)	0.876/0.765	0.913/0.781
GOOF (based on F^2)	1.001	1.000
R factors (based on reflections with $I > 2\sigma(I)$)		
R_1	0.0298	0.0337
wR_2	0.0662	0.0710
R factors (based on all reflections)		
R_1	0.0520	0.0620
wR_2	0.0697	0.0749
$\Delta\rho_{\max}/\Delta\rho_{\min}, \text{e}\text{\AA}^{-3}$	0.340/-0.265	0.462/-0.536