Supporting information

Photolysis of Diarylvinylcyclopropenes for the Construction of 1-Methylene-8a-aryl-1,8a-dihydroazulene Skeletons

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CONTENTS

1. General Remarks. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

2. UV spectroscopic data for substrates 1

Compound 1a: This is a known compound.[1] $\lambda_{1(max)}$ = 358 nm (ε_1 = 28894), $\lambda_{2(max)}$ = 250 nm (ε_2 = 9621).

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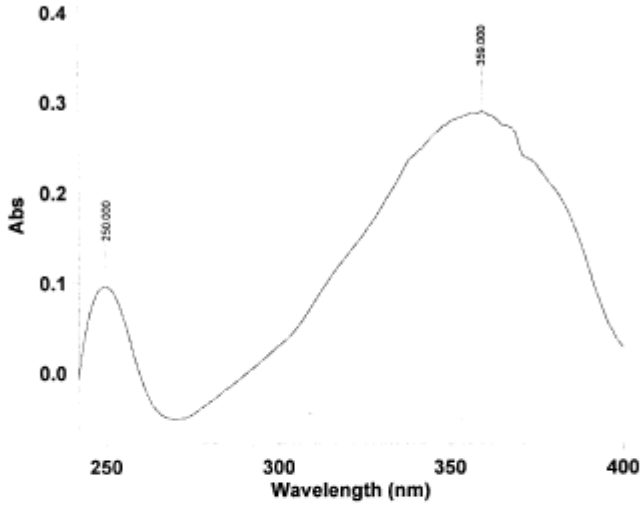
Varian cary 500 UV-Vis-NIR Spectrophotometer



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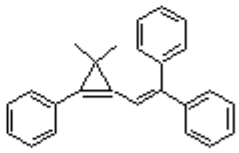

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Peak Table
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Peak Threshold 0.01000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
359.000	0.28894
250.000	0.09621

Compound 1b: This is a known compound.[1] $\lambda_{1(max)}$ = 366 nm (ε_1 = 44623), $\lambda_{2(max)}$ = 252 nm (ε_2 = 10535).

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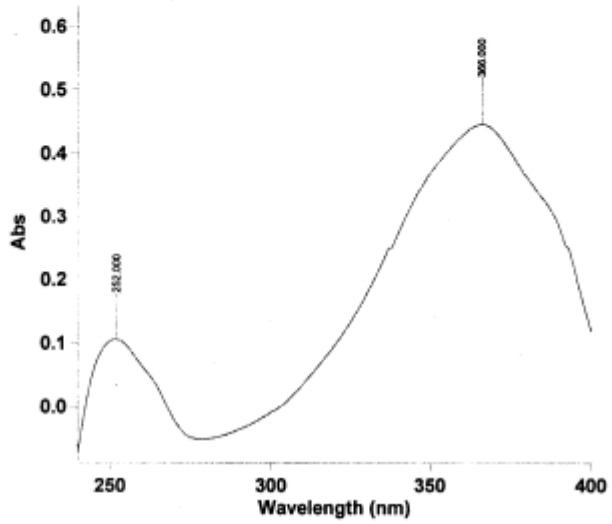

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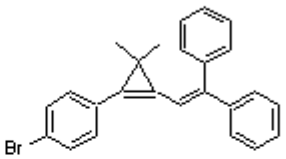

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Wavelength (nm)	Abs
366.000	0.44623
252.000	0.10535

Compound 1c: This is a known compound.[1] $\lambda_{1(max)}$ = 366 nm (ε_1 = 32974), $\lambda_{2(max)}$ = 252 nm (ε_2 = 10048).

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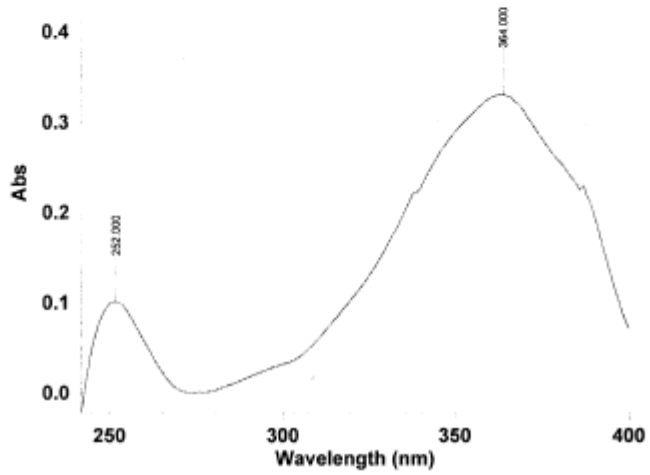

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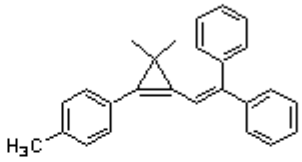

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Peak Table
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Peak Threshold 0.01000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
364.000	0.32974
252.000	0.10048

Compound 1d: This is a known compound.[1] $\lambda_{1(max)}$ = 366 nm (ε_1 = 56844), $\lambda_{2(max)}$ = 253 nm (ε_2 = 31357).

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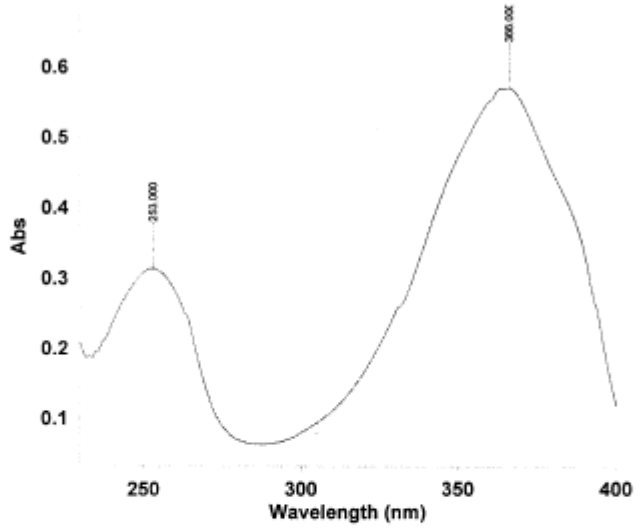

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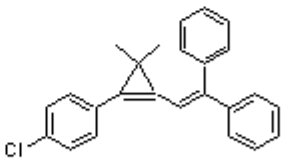

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Peak Table
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Peak Threshold 0.01000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
366.000	0.56844
253.000	0.31357

Compound 1e: This is a known compound.[1] $\lambda_{1(max)}$ = 358.5 nm (ε_1 = 23762), $\lambda_{2(max)}$ = 252.5 nm, (ε_2 = 30435).

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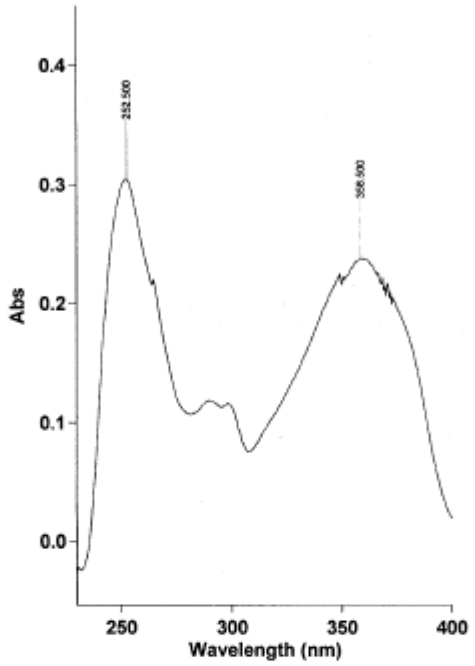

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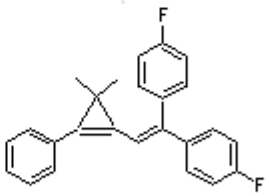

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Peak Table
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Peak Threshold 0.05000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
358.500	0.23762
252.500	0.30435

Compound 1f: This is a known compound.[1] $\lambda_{(max)}$ = 363 nm (ε_1 = 39196).

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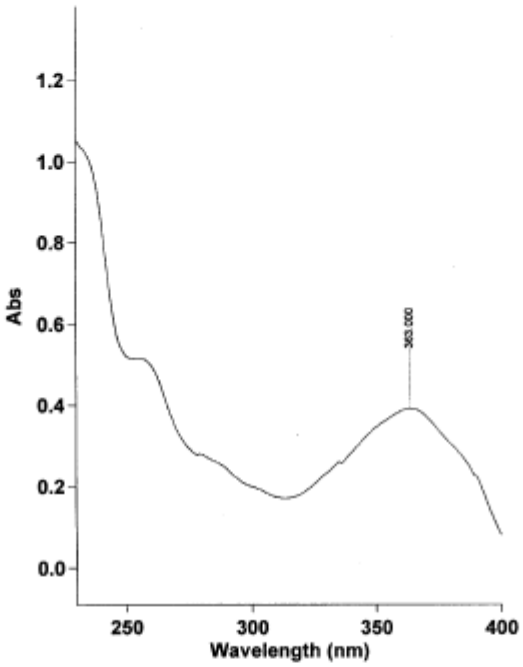
Varian cary 500 UV-Vis-NIR Spectrophotometer



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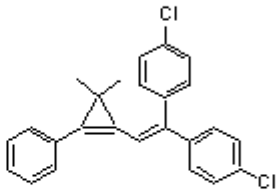

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Peak Table
Peak Style Peaks
Peak Threshold 0.00600
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
363.000	0.39196

Compound 1g: This is a known compound.[1] $\lambda_{1(max)}$ = 358 nm (ε$_1$ = 9605), $\lambda_{2(max)}$ = 258 nm (ε$_2$ = 57599).

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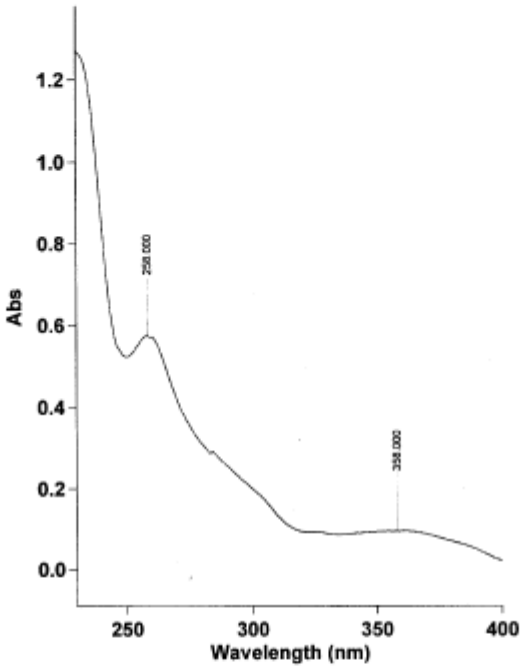
Varian cary 500 UV-Vis-NIR Spectrophotometer



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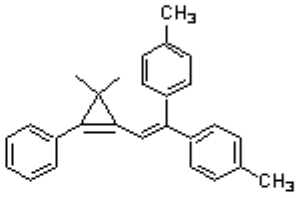

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Collection Time 2007-7-2 16:43:18

Peak Table
Peak Style Peaks
Peak Threshold 0.00600
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
358.000	0.09605
258.000	0.57599

Compound 1h: This is a known compound.[1] $\lambda_{1(max)}$ = 357 nm (ε_1 = 11770), $\lambda_{2(max)}$ = 248 nm (ε_2 = 17956).

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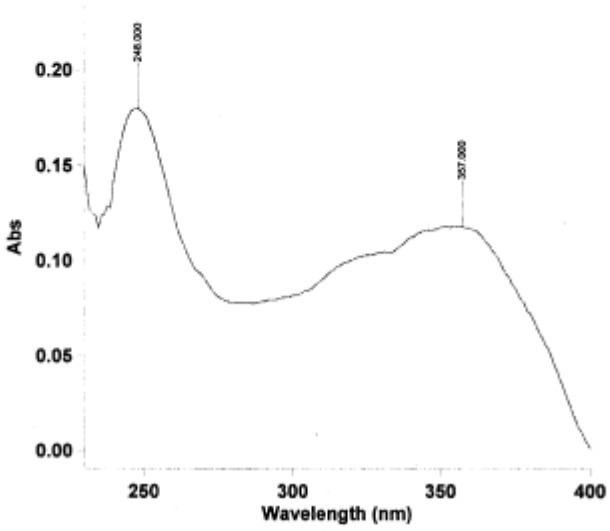
Varian cary 500 UV-Vis-NIR Spectrophotometer



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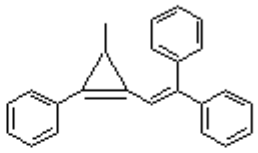

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Peak Table
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Peak Threshold 0.01000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
357.000	0.11770
248.000	0.17956

Compound 1i: This is a known compound.[1] $\lambda_{1(max)}$ = 366 nm (ε_1 = 33196), $\lambda_{2(max)}$ = 252 nm (ε_2 = 13743).

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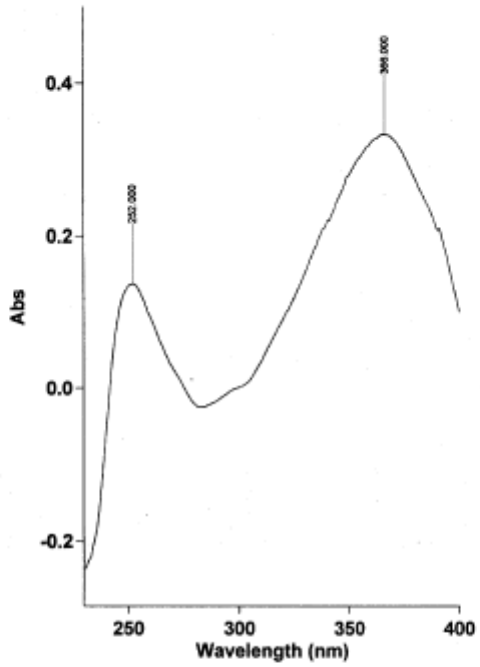
Varian cary 500 UV-Vis-NIR Spectrophotometer



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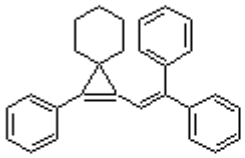

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Peak Table
Peak Style Peaks
Peak Threshold 0.01000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
366.000	0.33196
252.000	0.13743

Compound 1j: This is a known compound.[1] $\lambda_{1(max)}$ = 366 nm (ε_1 = 39280), $\lambda_{2(max)}$ = 250 nm (ε_2 = 5358).

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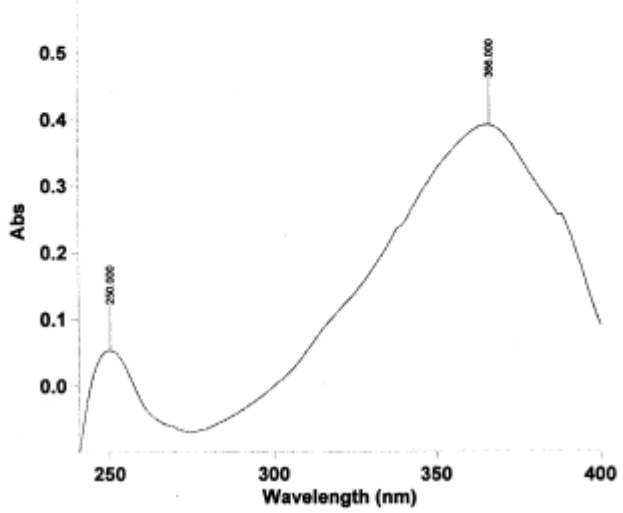
Varian cary 500 UV-Vis-NIR Spectrophotometer



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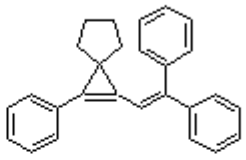

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Collection Time 2007-6-4 15:52:36

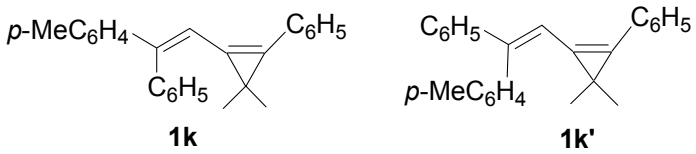
Peak Table
Peak Style Peaks
Peak Threshold 0.01000
Range 400.000nm to 230.000nm

Wavelength (nm)	Abs
366.000	0.39280
250.000	0.05358

3. Typical reaction procedure

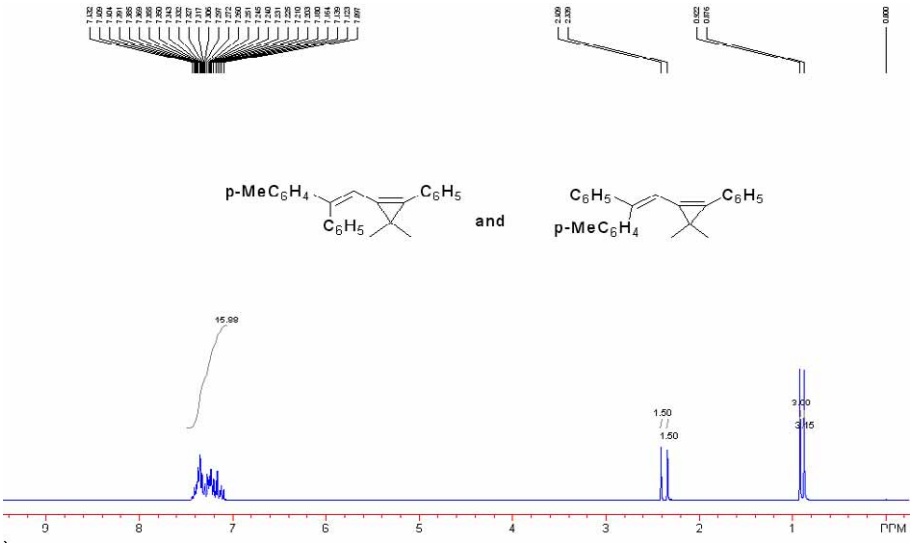
Typical reaction procedure for the photorearrangement of vinylcyclopropene 1a: A solution of vinylcyclopropenes **1a** (32 mg, 0.1 mmol) in dichloromethane (5.0 mL) was irradiated in a Pyrex tube by a 300 W high pressure mercury lamp for 7 h. After the starting materials were consumed (monitored by TLC), the solution was condensed under reduced pressure and the residue was purified by a flash column chromatography to yield the desired product **2a** (25.9 mg, 81%) as a yellow oil.

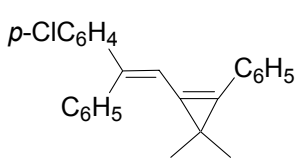
4. Spectroscopic data of substrates 1k, 1k', 1l, 1l' and products 2



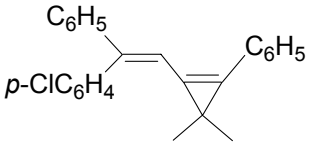
1k **1k'**

A yellow oil. (compound **1k** or **1k'** (1:1)) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.88 (s, 3H), 0.92 (s, 3H), 2.34 (s, 3H), 7.10-7.44 (m, 15). (compound **1k'** or **1k**) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.88 (s, 3H), 0.92 (s, 3H), 2.41 (s, 3H), 7.10-7.44 (m, 15). IR (CH_2Cl_2) ν 3056, 3023, 2958, 2923, 2854, 1769, 1595, 1509, 1486, 1445, 1361, 1238, 1174, 1066, 875, 817, 760, 743, 690, 609 cm^{-1}. UV (CH_2Cl_2): λ_{max} = 360 nm (ε = 10580). MS (%) m/z 336 (M^+, 88), 321 (100), 306 (28), 337 (21), 229 (20), 243 (19), 205 (14), 291 (15), 131 (13), 215 (11). HRMS (EI) calcd. for $C_{26}H_{24}$: 336.1878, Found: 336.1878.



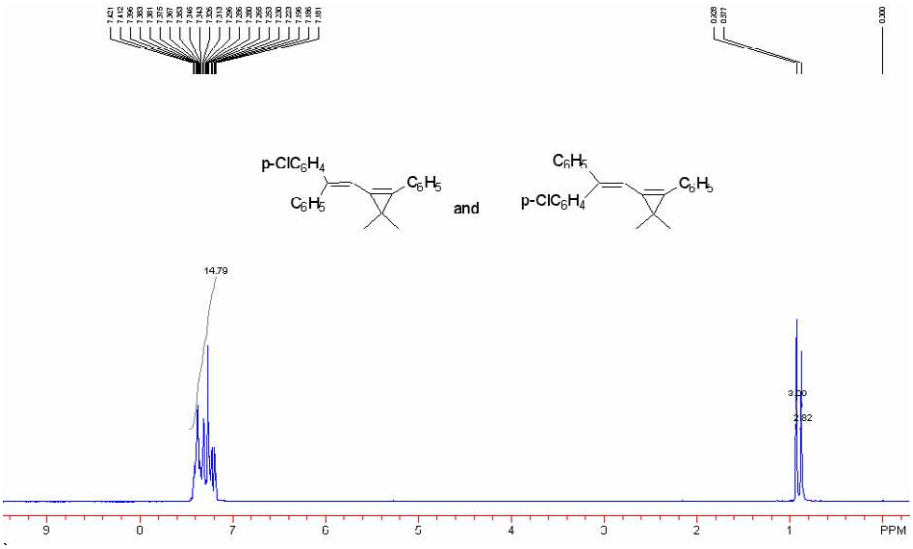


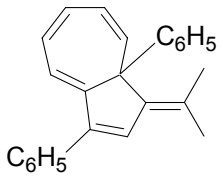
1l



1l'

A yellow solid, Mp: 108-110 ^{o}C. (compound **1l** or **1l'** (1:1)) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.88 (s, 6H), 7.18-7.42 (m, 15H). (compound **1l'** or **1l**) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.93 (s, 6H), 7.18-7.42 (m, 15H). IR (CH_2Cl_2) ν 3076, 3058, 3025, 2960, 2922, 2854, 1937, 1899, 1771, 1594, 1567, 1485, 1444, 1402, 1362, 1175, 1090, 1071, 1028, 1015, 910, 880, 827, 777, 761, 724, 691, 608, 569, 495 cm^{-1}. UV (CH_2Cl_2): $\lambda_{1(maz)}$ = 360 nm (ε_1 = 4750), $\lambda_{2(max)}$ = 258 nm (ε_2 = 35915). MS (%) m/z 358 (M^++2, 28), 356 (M^+, 100), 341 (78), 306 (38), 131 (25), 291 (22), 229 (20), 228 (14), 263 (15), 91 (16), 201 (11), 289 (11), 321 (11). HRMS (EI) calcd. for $C_{25}H_{21}Cl$: 358.1302, 356.1332, Found: 358.1338, 356.1332.

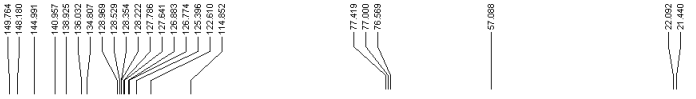


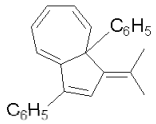


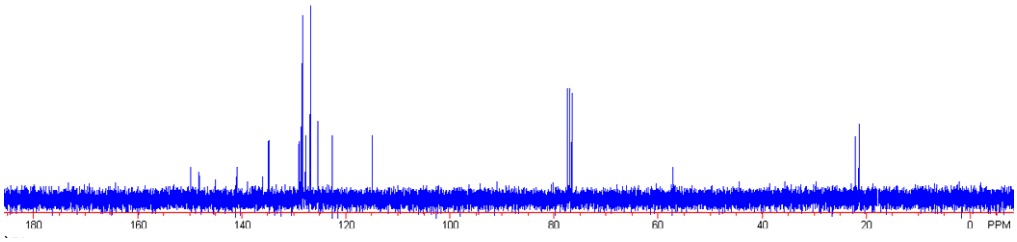
2a

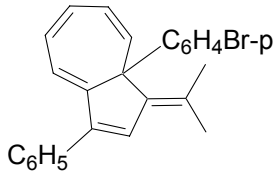
A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.61 (s, 3H), 1.89 (s, 3H), 5.79 (d, J = 9.9 Hz,1H), 6.18-6.33 (m, 3H), 6.58 (dd, J = 10.2, 6.3 Hz, 1H), 6.83 (s, 1H), 7.00-7.11 (m, 3H), 7.15-7.19 (m, 2H), 7.31-7.43 (m, 3H), 7.49-7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.4, 22.1, 57.1, 114.9, 122.6, 125.4, 126.8, 126.9, 127.6, 127.8, 128.2, 128.4, 128.5, 129.0,

134.8, 136.0, 138.9, 141.0, 145.0, 148.2, 149.8. IR (CH_2Cl_2) ν 3057, 3023, 2968, 2925, 2854, 1598, 1492, 1445, 1376, 1156, 1073, 1029, 764, 731, 702 cm^{-1}. MS (%) m/z 322 (M^+, 100), 307 (88), 229 (50), 245 (46), 215 (45), 292 (41), 291 (23), 202 (24), 323 (23), 279 (15), 91 (16). HRMS (EI) calcd. for $C_{25}H_{22}$: 322.1722, Found: 322.1721.





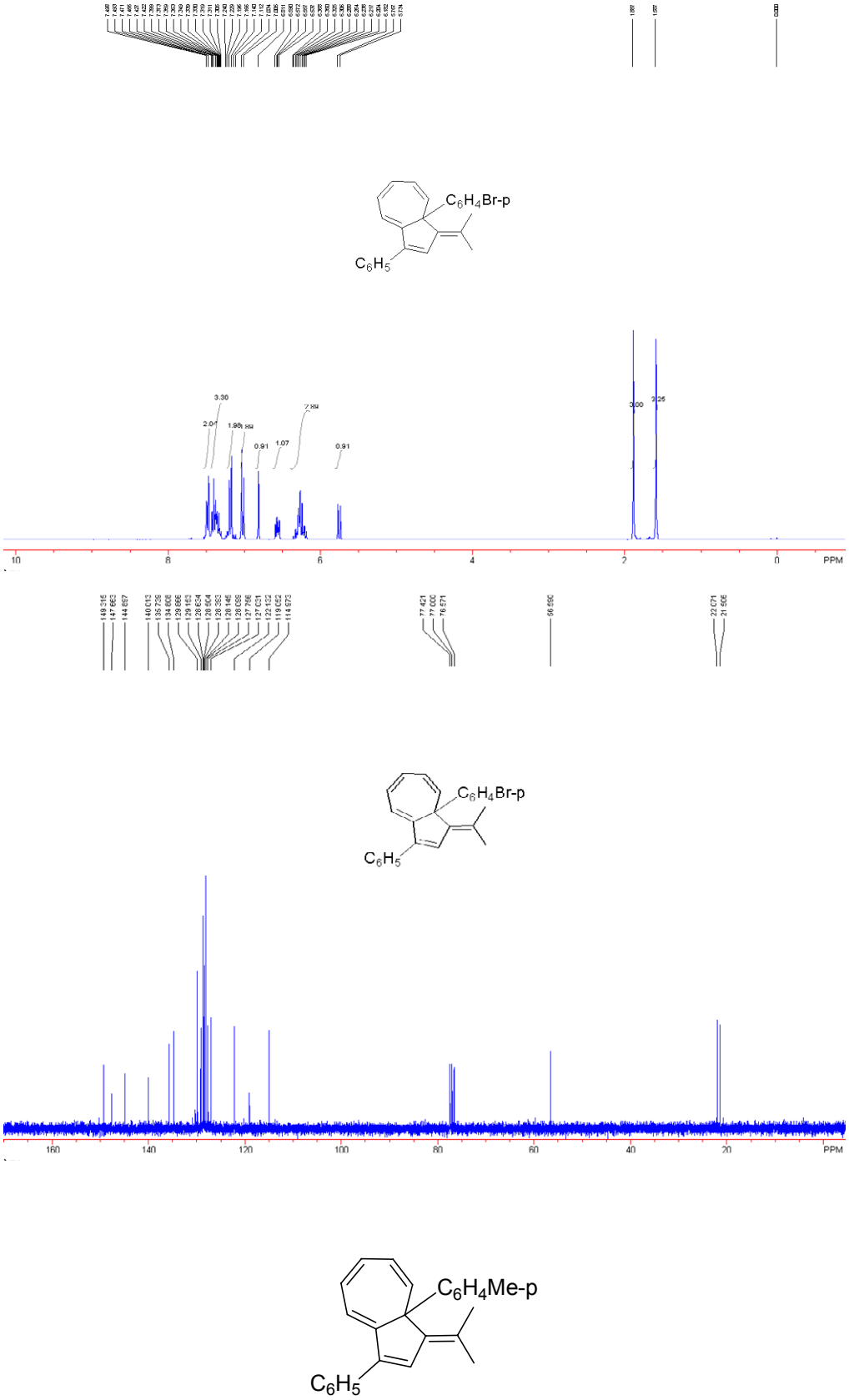




2b

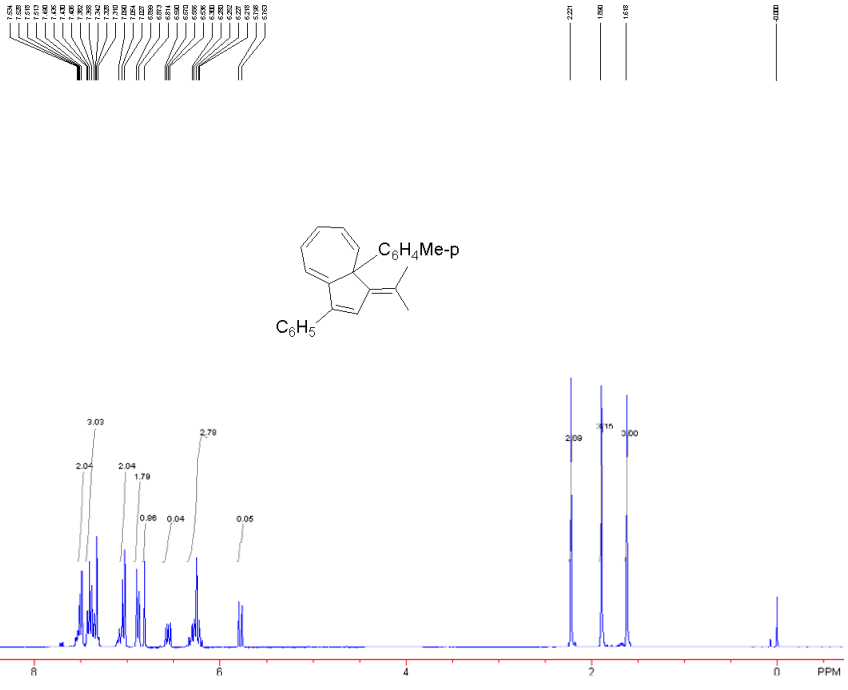
A yellow solid, Mp: 170 °C (decomposed). ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.59 (s, 3H), 1.89 (s, 3H), 5.75 (d, *J* = 10.2 Hz, 1H), 6.18-6.33 (m, 3H), 6.56 (dd, *J* = 10.2, 5.7 Hz, 1H), 6.81 (s, 1H), 7.02 (dd, *J* = 9.0, 2.4 Hz, 2H), 7.18 (dd, *J* = 9.0, 2.4 Hz, 2H), 7.32-7.43 (m, 3H), 7.47-7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 22.1, 56.6, 115.0, 119.1, 122.1, 127.0, 127.8, 128.10, 128.15, 128.4, 128.5, 128.6, 129.2, 129.9, 134.8, 135.7, 140.0, 144.9, 147.7, 149.3. IR (CH_2Cl_2) ν 3055, 3023, 2923, 2852, 1638, 1600, 1484, 1443, 1392, 1372, 1072, 1010, 871, 817, 777, 765, 710, 699, 682, 648, 632, 605, 507 cm^{-1}. MS (%) m/z 402 (M^++2, 73), 400 (M^+, 87), 306 (100), 291 (79), 245 (57), 229 (41), 215 (33), 385 (32), 307 (26), 289 (21), 321 (21), 202 (20). HRMS (EI) calcd. for $C_{25}H_{21}Br$: 402.0806, 400.0827,

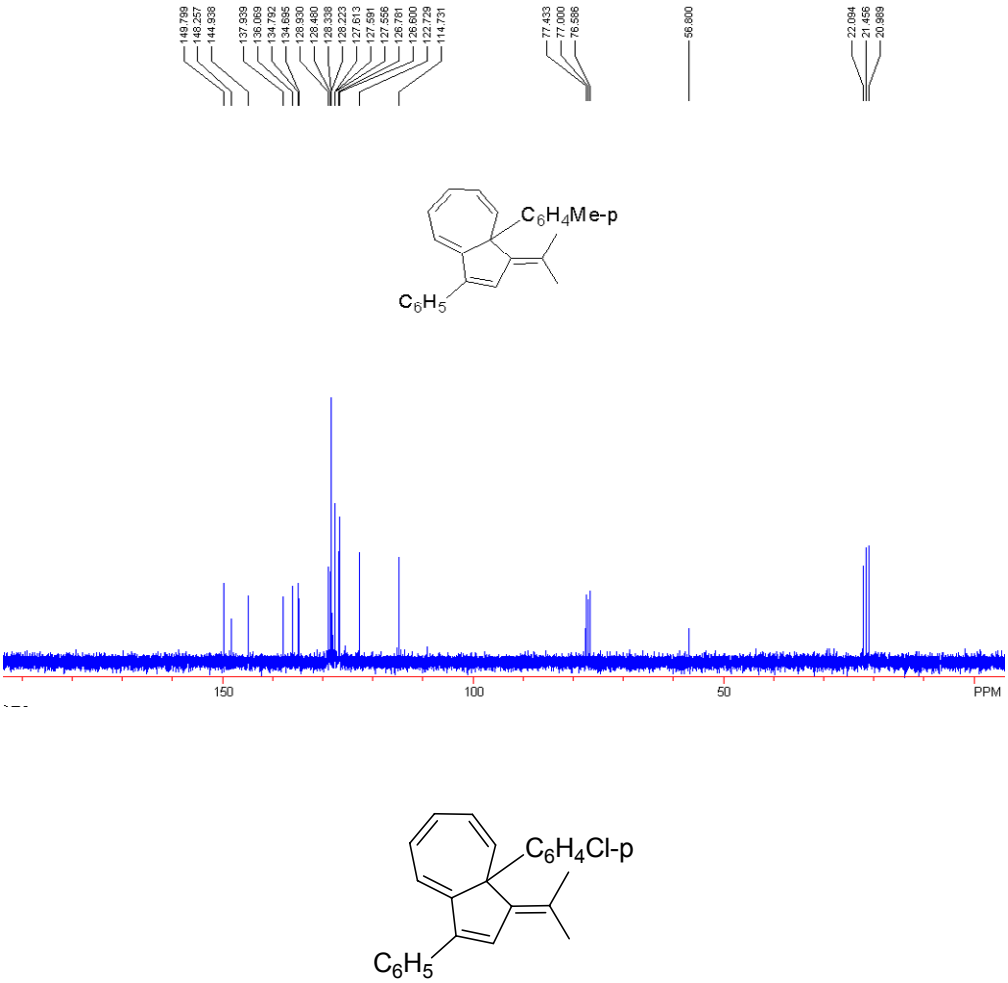
Found: 402.0874, 400.0819.



2c

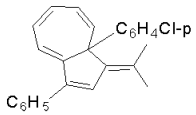
A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.62 (s, 3H), 1.89 (s, 3H), 2.22 (s, 3H), 5.78 (d, *J* = 10.2 Hz, 1H), 6.22-6.30 (m, 3H), 6.56 (dd, *J* = 10.2, 6.0 Hz, 1H), 6.82 (s, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 7.03-7.09 (m, 2H), 7.33-7.43 (m, 3H), 7.49-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.0, 21.5, 22.1, 56.8, 114.7, 122.7, 126.6, 126.8, 127.56, 127.59, 127.6, 128.2, 128.3, 128.5, 128.9, 134.7, 134.8, 136.1, 137.9, 144.9, 148.3, 149.8. IR (CH_2Cl_2) ν 3019, 2927, 2854, 1731, 1633, 1602, 1509, 1488, 1444, 1377, 1272, 1121, 1073, 1022, 874, 813, 766, 725, 711, 701 cm^{-1}. MS (%) m/z 336 (M^+, 100), 321 (79), 306 (45), 291(34) 229 (32), 245 (31), 337 (27), 215 (21), 202 (14), 289 (13), 279. HRMS (EI) calcd. for $C_{26}H_{24}$: 336.1878, Found: 336.1879.

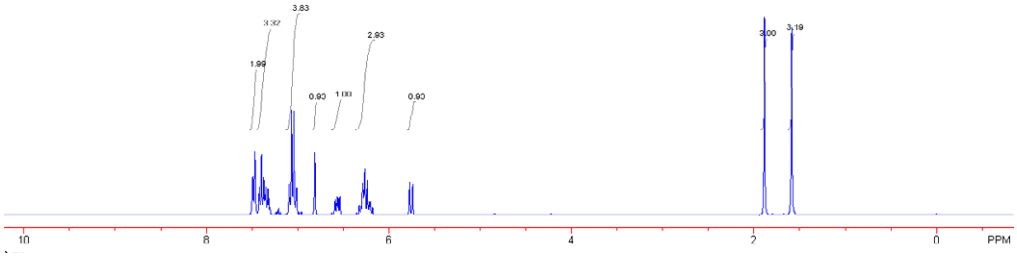


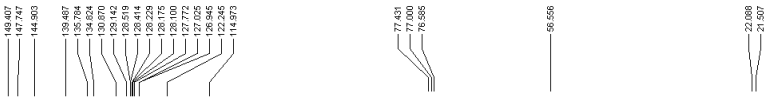


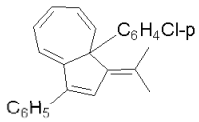
2d

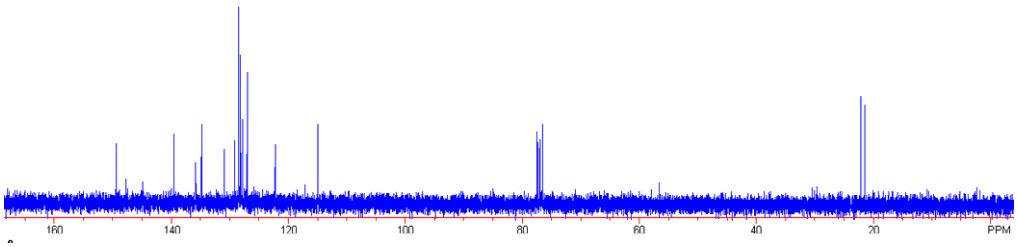
A yellow solid, Mp: 159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.59 (s, 3H), 1.89 (s, 3H), 5.75 (d, *J* = 10.2 Hz, 1H), 6.18-6.33 (m, 3H) 6.56 (dd, *J* = 10.2, 6.0 Hz, 1H), 6.81 (s, 1H), 7.01-7.09 (m, 4H), 7.30-7.42 (m, 3H), 7.47-7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 22.1, 56.5, 115.0, 122.2, 126.9, 127.0, 127.8, 128.1, 128.18, 128.23, 128.4, 128.5, 129.1, 130.9, 134.8, 135.8, 139.5, 144.9, 147.7, 149.4. IR (CH_2Cl_2) ν 3021, 2922, 2853, 1636, 1601, 1487, 1444, 1398, 1373, 1093, 1014, 820, 777, 766, 725, 711, 701 cm^{-1}. MS (%) m/z 358 (M+2, 34), 356 (M^+, 100), 291 (64), 306 (57), 341 (49), 245 (49), 229 (33), 215 (28), 321 (24), 202 (16), 289 (16). HRMS (EI) calcd. for $C_{25}H_{21}Cl$: 358.1302, 356.1332, Found: 358.1326, 356.1332.

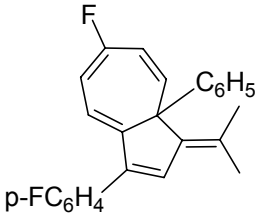

C6H4Cl-p
C6H5


3.83
2.93
1.99
0.93
1.00
0.93
3.00
3.19
10
8
6
4
2
0
PPM



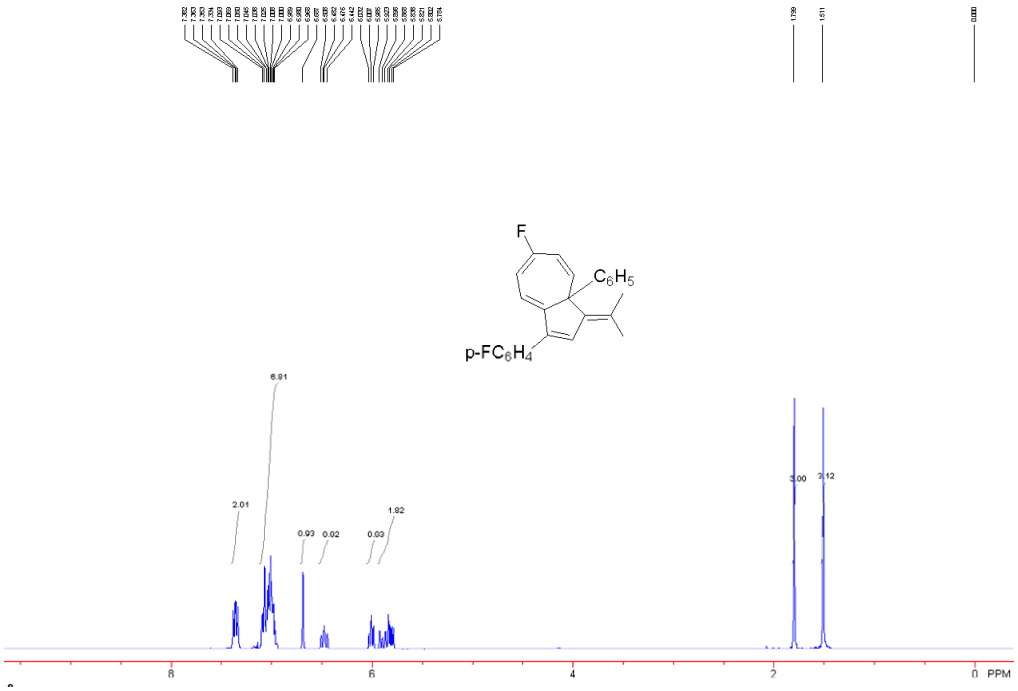

C6H4Cl-p
C6H5

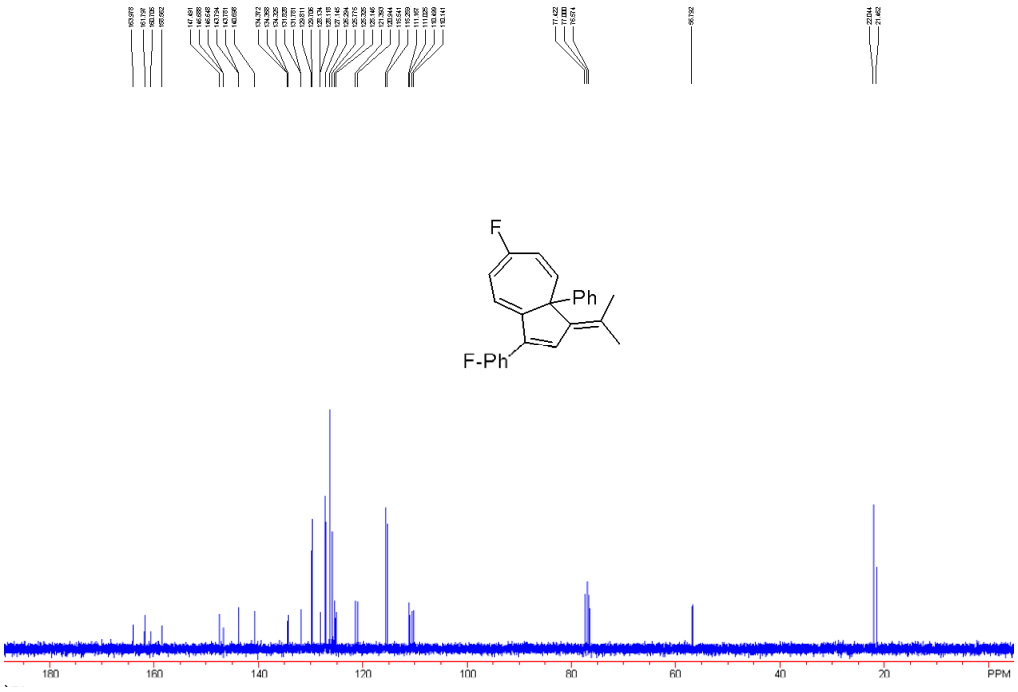

160
140
120
100
80
60
40
20
PPM

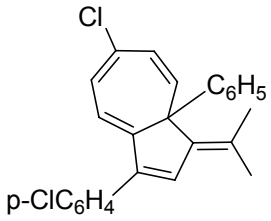

F
C6H5
p-FC6H4

2e

A yellow solid, Mp: 120 °C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.51 (s, 3H), 1.80 (s, 3H), 5.78-5.92 (m, 2H), 6.00 (t, J = 6.9 Hz, 1H), 6.44-6.51 (m, 1H), 6.69 (s, 1H), 6.94-7.10 (m, 7H), 7.33-7.38 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 22.0, 56.8, 110.3 (d, $J_{C\text{-}F}$ = 26.2 Hz), 111.1 (d, $J_{C\text{-}F}$ = 10.7 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 121.2 (d, $J_{C\text{-}F}$ = 33.6 Hz), 125.2 (d, $J_{C\text{-}F}$ = 13.4 Hz), 125.8, 126.3, 127.1, 128.1, 129.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 131.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 134.4, (d, $J_{C\text{-}F}$ = 3.5 Hz), 140.7, 143.8, 146.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 147.5, 160.2 (d, $J_{C\text{-}F}$ = 242.6 Hz), 162.3 (d, $J_{C\text{-}F}$ = 245.5 Hz). IR (CH_2Cl_2) ν 3056, 3028, 2913, 2854, 1711, 1627, 1604, 1501, 1446, 1415, 1223, 1157, 1124, 863, 838, 801, 761, 747, 712, 702, 579 cm^{-1}. MS (%) m/z 358 (M^+, 100), 343 (51), 281 (33), 328 (28), 327 (22), 359 (22), 233 (15), 247 (14), 323 (12), 220 (8), 282 (7). HRMS (EI) calcd. for $C_{25}H_{20}F_2$: 358.1533, Found: 358.1535.

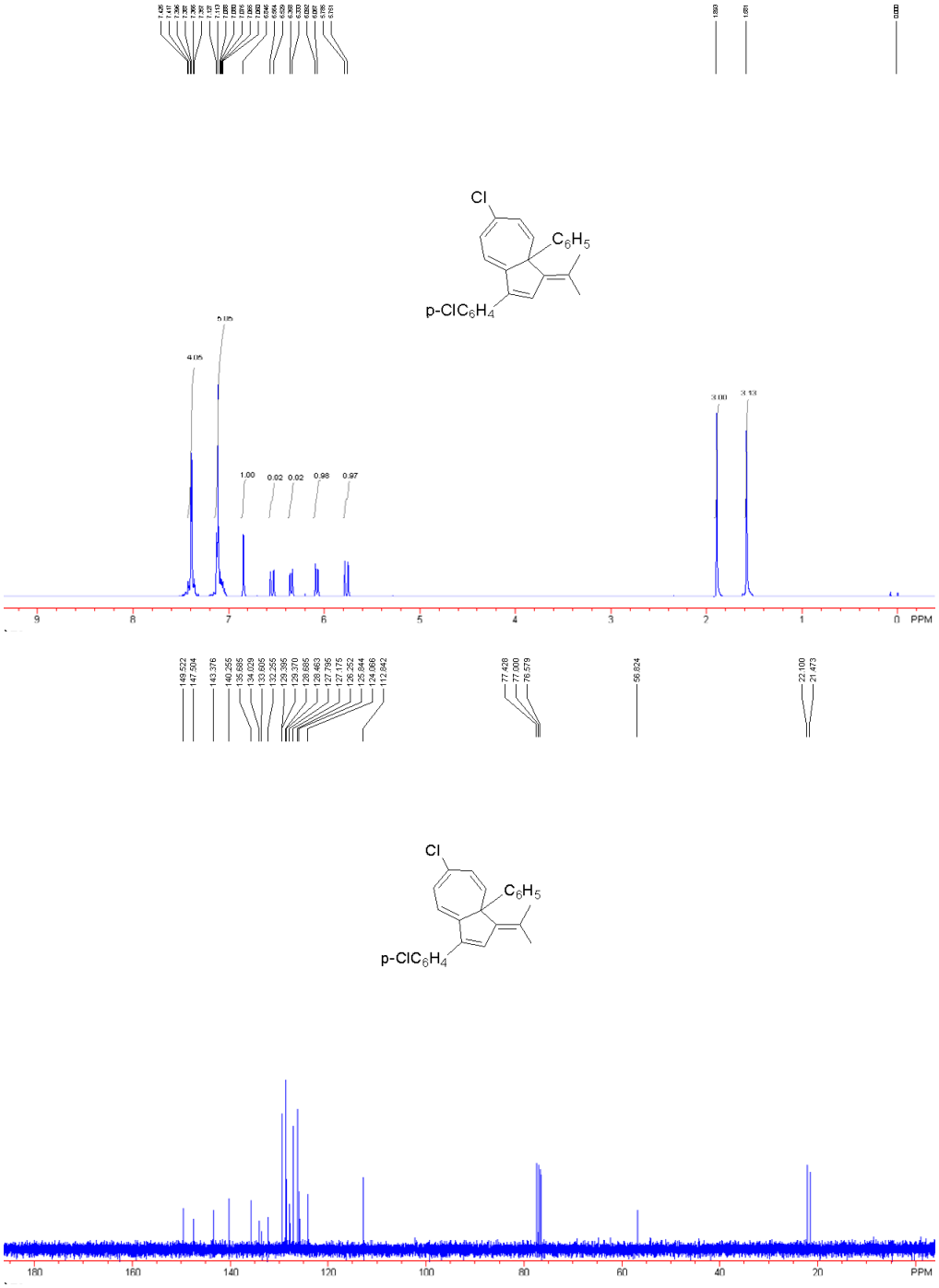




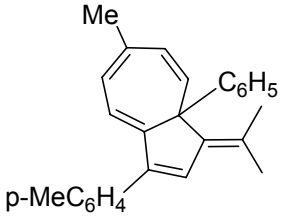


2f

A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.58 (s, 3H), 1.89 (s, 3H), 5.77 (d, J = 10.8 Hz, 1H), 6.08 (d, J = 7.5 Hz, 1H), 6.35 (d, J = 7.2 Hz, 1H), 6.55 (d, J = 10.2 Hz, 1H), 6.85 (s, 1H), 7.08-7.13 (m, 5H), 7.36-7.43 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 22.1, 56.8, 112.8, 124.1, 125.8, 126.3, 127.2, 127.8, 128.5, 128.7, 129.37, 129.40, 132.3, 133.6, 134.0, 135.7, 140.3, 143.4, 147.5, 149.5. IR (CH_2Cl_2) ν 3059, 3026, 2957, 2926, 2855, 1726, 1662, 1601, 1487, 1446, 1400, 1274, 1090, 1014, 831, 760, 702 cm^{-1}. MS (%) m/z 394 (M^++4, 8), 392 (M^++2, 41), 390 (M^+, 65), 278 (100), 348 (76), 313 (62), 276 (55), 350 (52), 340 (38), 325 (34), 279 (33), 375 (26). HRMS (EI) calcd. for $C_{25}H_{20}Cl_2$: 394.0883, 392.0913, 390.0942, Found: 394.0914, 392.0942, 390.0923.

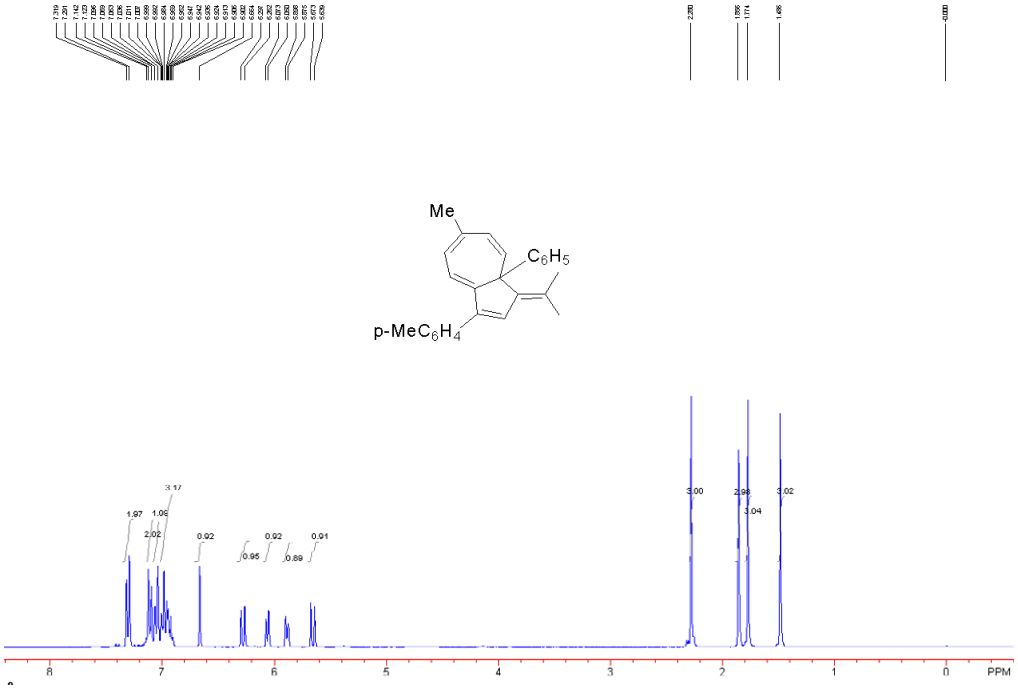

Cl
C6H5
p-ClC6H4
1.00
0.02
0.02
0.98
0.97
PPM

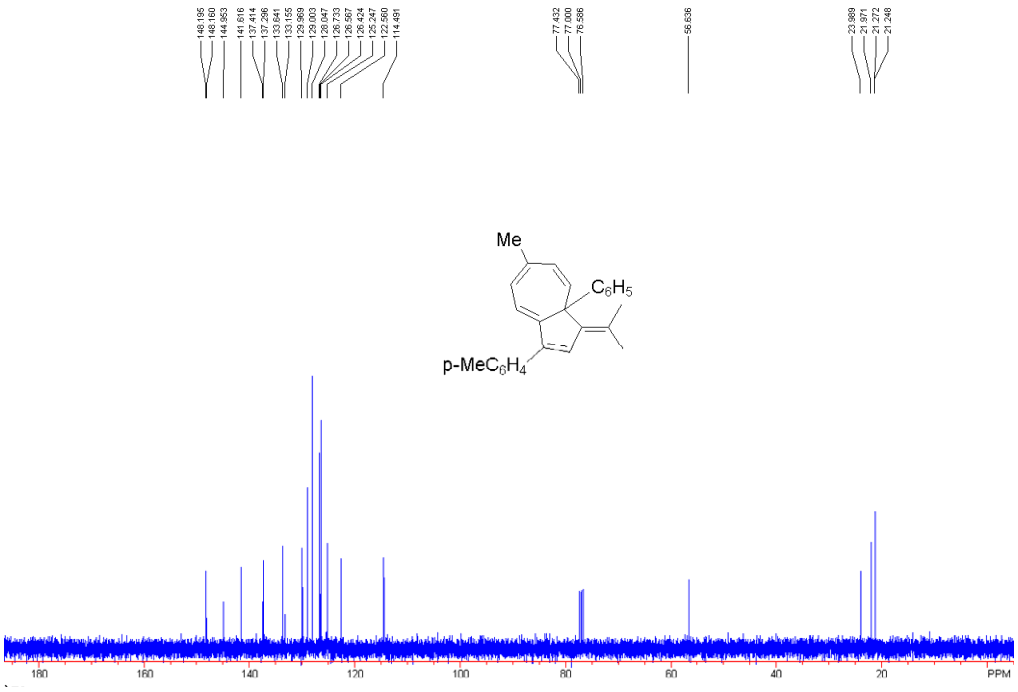
Cl
C6H5
p-ClC6H4
PPM

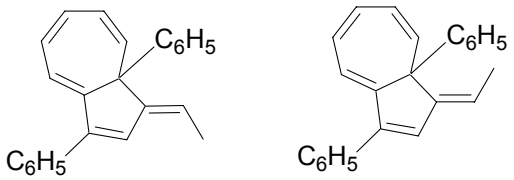

Me
C6H5
p-MeC6H4

2g

A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.49 (s, 3H), 1.78 (s, 3H), 1.86 (s, 3H), 2.28 (s, 3H), 5.66 (d, *J* = 9.9 Hz, 1H), 5.89 (d, *J* = 6.6 Hz, 1H), 6.06 (d, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 10.2 Hz, 1H), 6.67 (s, 1H), 6.90-7.01 (m, 3H), 7.04-7.07 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.2, 21.3, 22.0, 24.0, 56.6, 114.5, 122.6, 125.2, 126.4, 126.6, 126.7, 128.0, 129.0, 130.0, 133.2, 133.6, 137.3, 137.4, 141.6, 145.0, 148.16, 148.20. IR (CH_2Cl_2) ν 3054, 3020, 2972, 2922, 2853, 1722, 1598, 1504, 1491, 1445, 1373, 1264, 1177, 1111, 1032, 821, 758, 702 cm^{-1}. MS (%) m/z 350 (M^+, 100), 335 (76), 305 (42), 320 (35), 273 (32), 351 (30), 243 (26), 229 (18), 257 (16). HRMS (EI) calcd. for $C_{27}H_{26}$: 350.2035, Found: 350.2035.

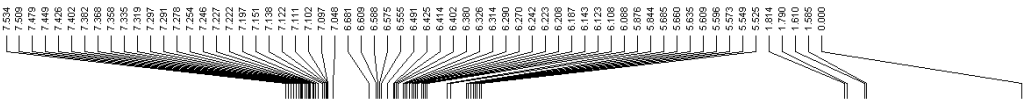


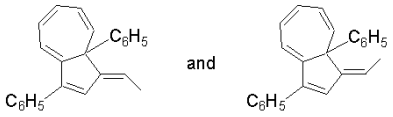


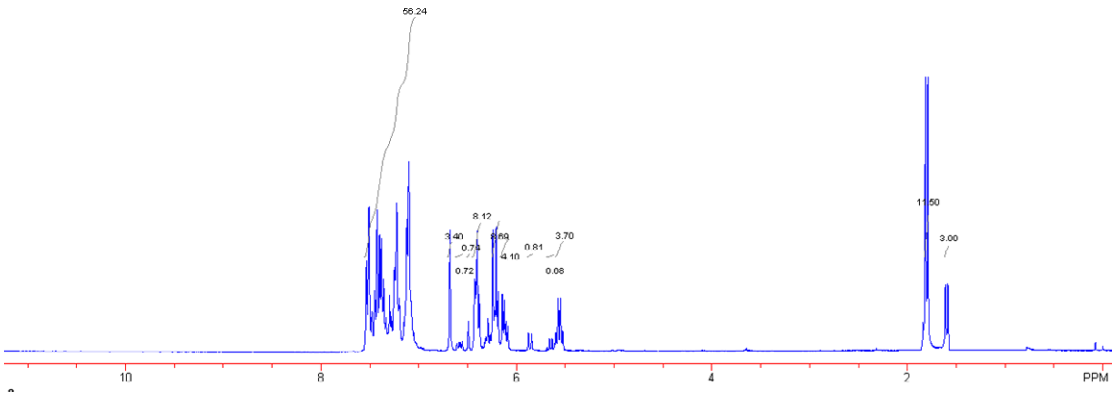


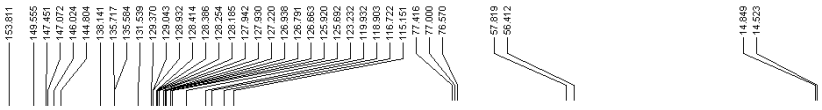
2h **2h'**

A yellow oil. (compound **2h** or **2h'** = 4:1) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.60 (d, *J* = 7.5 Hz, 3H), 5.65 (dd, *J* = 7.5, 15.2 Hz, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 6.19-6.31 (m, 2H), 6.38-6.42 (m, 1H), 6.49 (s, 1H), 6.58 (dd, *J* = 10.1, 6.0 Hz, 1H), 7.05-7.53 (m, 10H). (compound **2h'** or **2h**) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.80 (d, *J* = 7.2 Hz, 3H), 5.56 (dd, *J* = 6.9, 14.3 Hz, 1H), 6.09-6.14 (m, 1H), 6.19-6.33 (m, 2H), 6.38-6.43 (m, 2H), 6.68(s, 1H), 7.05-7.53 (m, 10H). (compound **2h** or **2h'**) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.8, 57.8, 116.7, 118.9, 125.7, 125.9, 126.7, 127.2, 127.9, 128.3, 128.4, 128.9, 129.4, 131.5, 135.7, 138.1, 144.8 147.1, 147.5, 153.8. (compound **2h'** or **2h**) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.6, 56.4, 115.2, 119.9, 123.2, 125.9, 126.8, 126.9, 127.9, 128.2, 128.4, 129.0, 129.4, 131.5, 135.6, 138.1, 144.8, 146.0, 149.6, 153.8. IR (CH_2Cl_2) ν 3056, 3023, 2924, 2852, 1718, 1598, 1445, 1362, 1265, 1027, 765, 699 cm^{-1}. MS (%) m/z 308 (M^+, 100), 293 (55), 215 (52), 291 (24), 278 (20), 216 (20), 231 (17), 202 (17) , 276 (16). HRMS (EI) calcd. for $C_{24}H_{20}$: 308.1565, Found: 308.1556.


7.534
7.529
7.479
7.449
7.426
7.402
7.382
7.368
7.358
7.335
7.319
7.297
7.291
7.278
7.254
7.246
7.227
7.222
7.187
7.151
7.138
7.122
7.111
7.102
7.097
7.046
6.681
6.609
6.588
6.575
6.555
6.491
6.425
6.414
6.400
6.380
6.326
6.314
6.290
6.270
6.242
6.223
6.208
6.187
6.143
6.123
6.108
6.088
5.876
5.844
5.665
5.650
5.635
5.609
5.596
5.573
5.549
5.525
1.814
1.790
1.610
1.585
0.000


C6H5
C6H5
and
C6H5
C6H5


56.24
8.12
3.40
0.75
0.72
4.10
0.81
3.70
0.08
11.50
3.00
10
8
6
4
2
PPM


153.811
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147.451
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146.024
144.804
138.141
135.717
135.584
131.539
129.370
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128.386
128.254
128.185
127.942
127.930
127.220
126.938
126.791
126.663
125.920
125.692
123.232
119.932
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116.722
115.151
77.416
77.000
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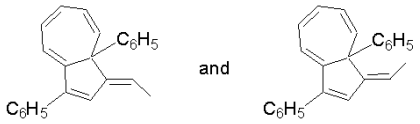
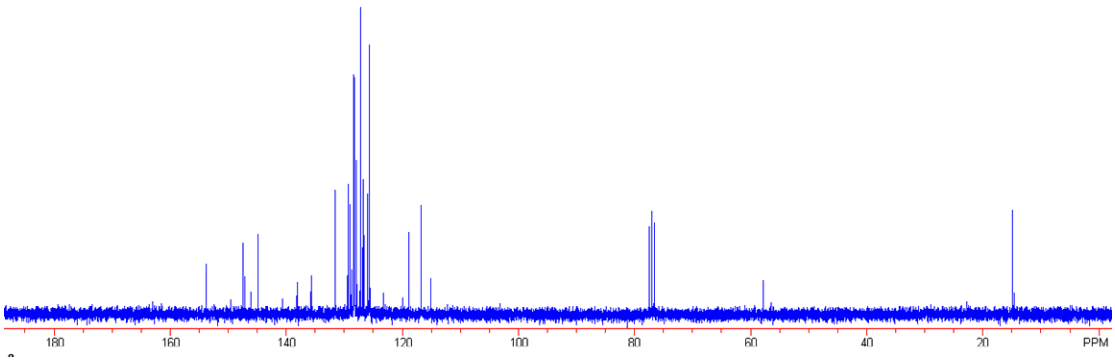
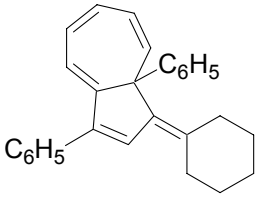
57.819
56.412
14.849
14.523

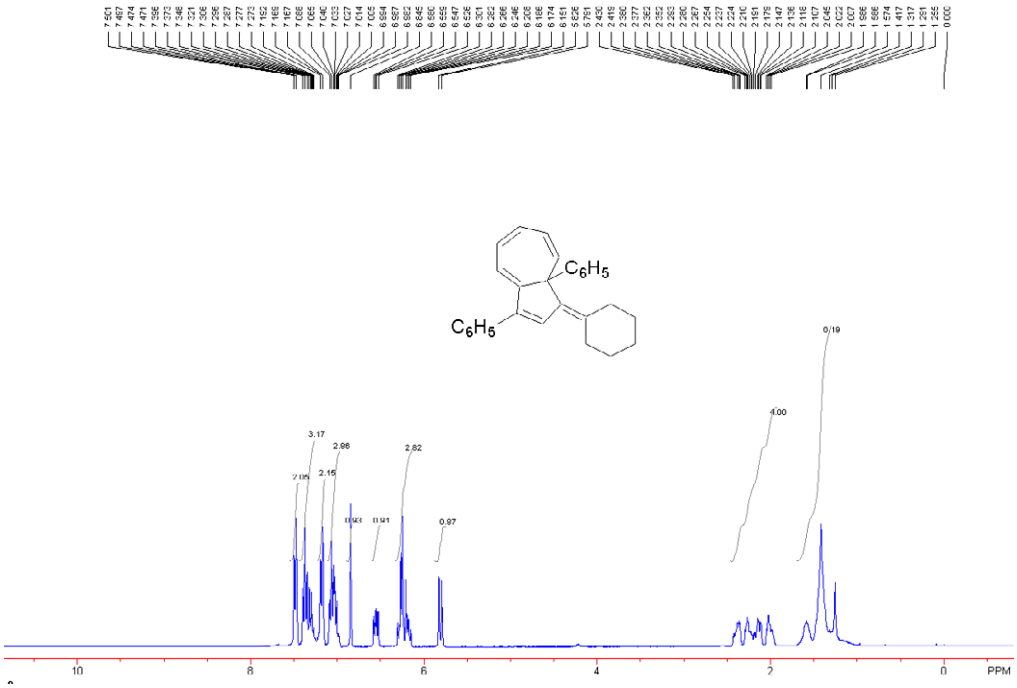

C6H5
C6H5
and
C6H5
C6H5

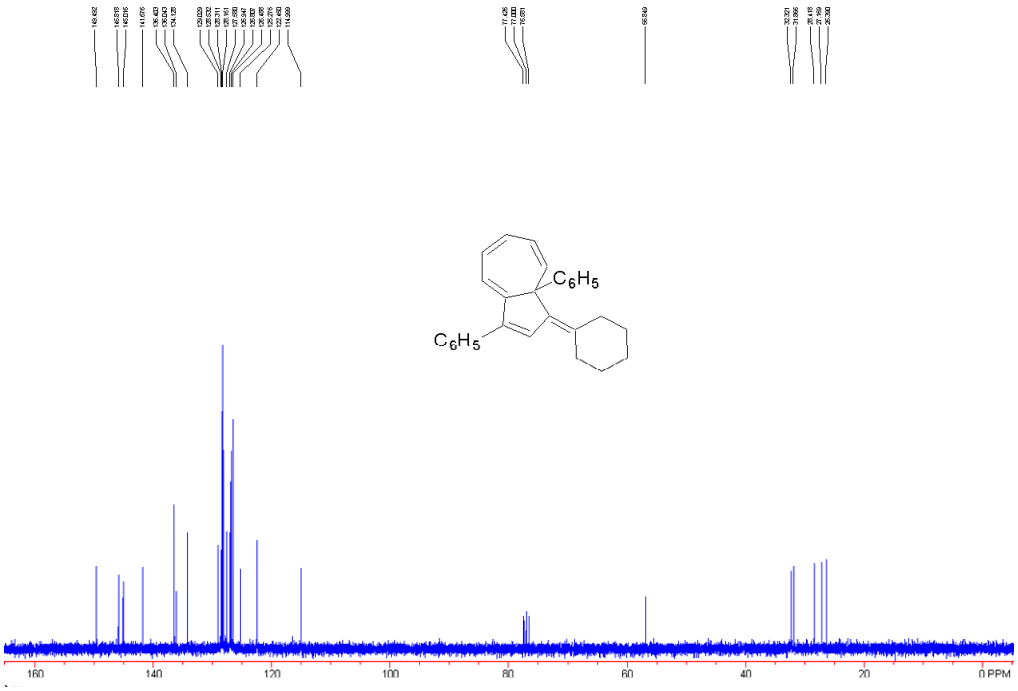

180
160
140
120
100
80
60
40
20
PPM

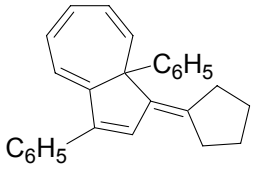


2i

A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.26-1.59 (m, 6H), 1.99-2.43 (m, 4H), 5.81 (d, J = 10.5 Hz, 1H), 6.15-6.30 (m, 3H), 6.55 (dd, J = 9.9, 6.3 Hz, 1H), 6.85 (s, 1H), 6.98-7.09 (m, 3H), 7.17-7.19 (m, 2H), 7.27-7.40 (m, 3H), 7.47-7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.4, 27.2, 28.4, 31.9, 32.3, 56.8, 115.0, 122.4, 125.3, 126.5, 126.8, 126.9, 127.6, 128.2, 128.3, 128.5, 129.0, 134.1, 136.0, 136.4, 141.7, 145.0, 145.8, 149.5. IR (CH_2Cl_2) ν 3055, 3019, 2926, 2852, 1632, 1599, 1490, 1445, 1349, 1265, 1174, 1071, 1028, 975, 875, 765, 754, 714, 700 cm^{-1}. MS (%) m/z 362 (M^+, 100), 280 (36), 360 (29), 217 (29), 293 (23), 215 (21), 305 (20), 279 (17), 202 (16), 278 (12), 319 (13). HRMS (EI) calcd. for $C_{28}H_{26}$: 362.2035, Found: 362.2036.

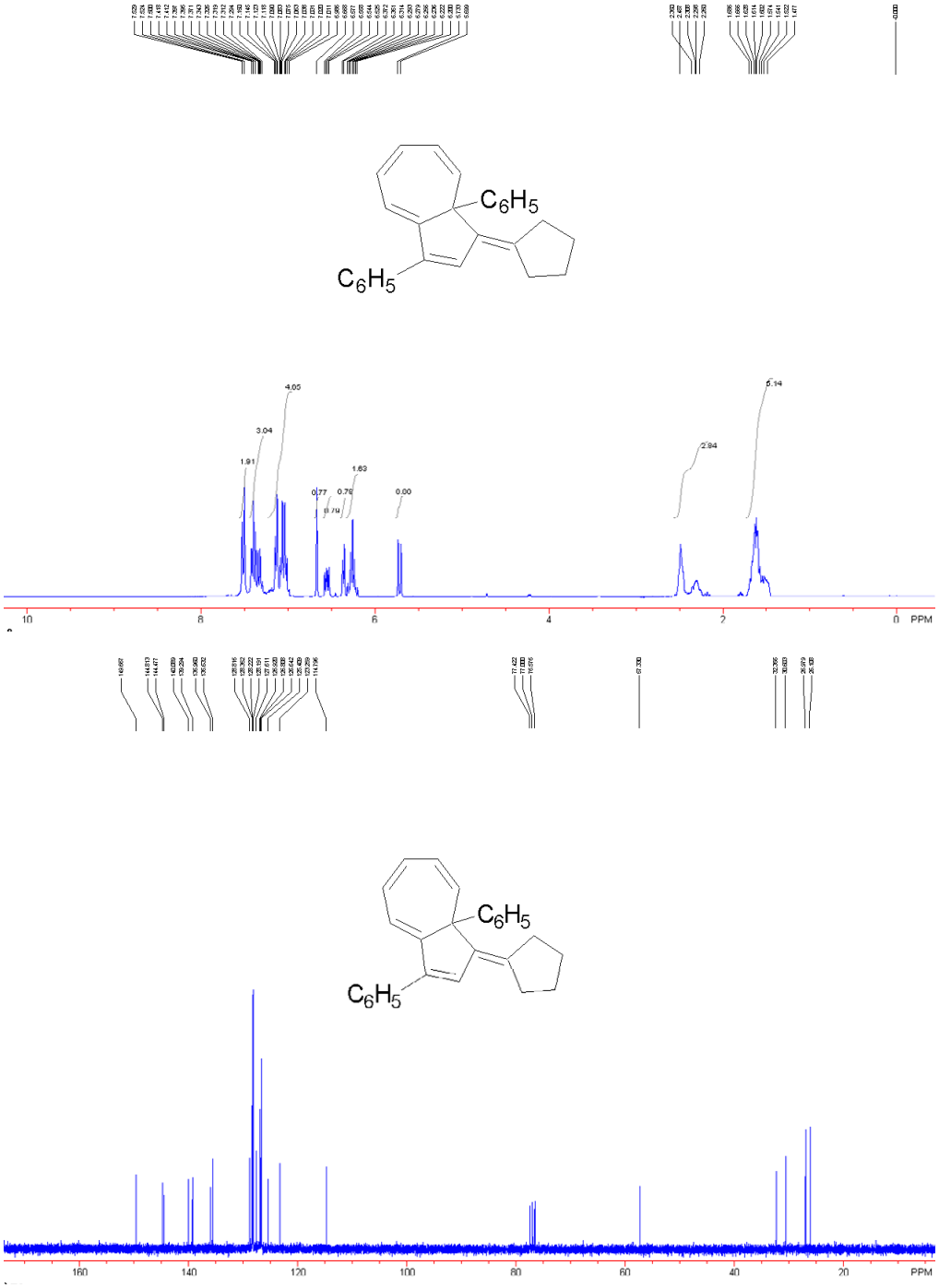


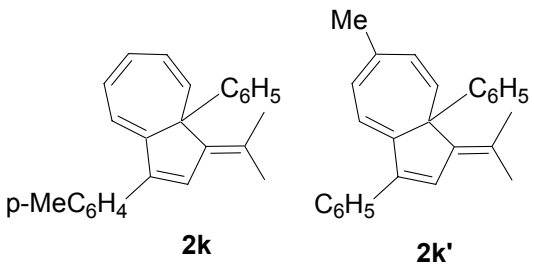




2j

A yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.48-1.69 (m, 4H), 2.16-2.49 (m, 4H), 5.72 (d, J = 9.9 Hz, 1H), 6.20-6.31 (m, 2H), 6.36 (d, J = 6.0 Hz, 1H), 6.55 (dd, J = 9.9, 5.7 Hz, 1H), 6.67 (s, 1H), 7.01-7.09 (m, 3H), 7.12-7.15 (m, 2H), 7.29-7.42 (m, 3H), 7.50-7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 26.1, 27.0, 30.6, 32.4, 57.3, 114.8, 123.3, 125.4, 126.6, 126.8, 126.9, 127.6, 128.19, 128.22, 128.4, 128.8, 135.6, 136.0, 139.3, 140.1, 144.5, 144.8, 149.7. IR (CH_2Cl_2) ν 3055, 3020, 2953, 2867, 2830, 1642, 1599, 1491, 1445, 1430, 1379, 1313, 1265, 1071, 1025, 876, 769, 766, 753, 741, 713, 700 cm^{-1}. MS (%) m/z 348 (M^+, 100), 346 (52), 280 (28), 271 (27), 305 (24), 215 (19), 229 (19), 257 (18), 167 (14), 202 (14), 241 (13), 317 (13). HRMS (EI) calcd. for $C_{27}H_{24}$: 348.1878, Found: 348.1878.

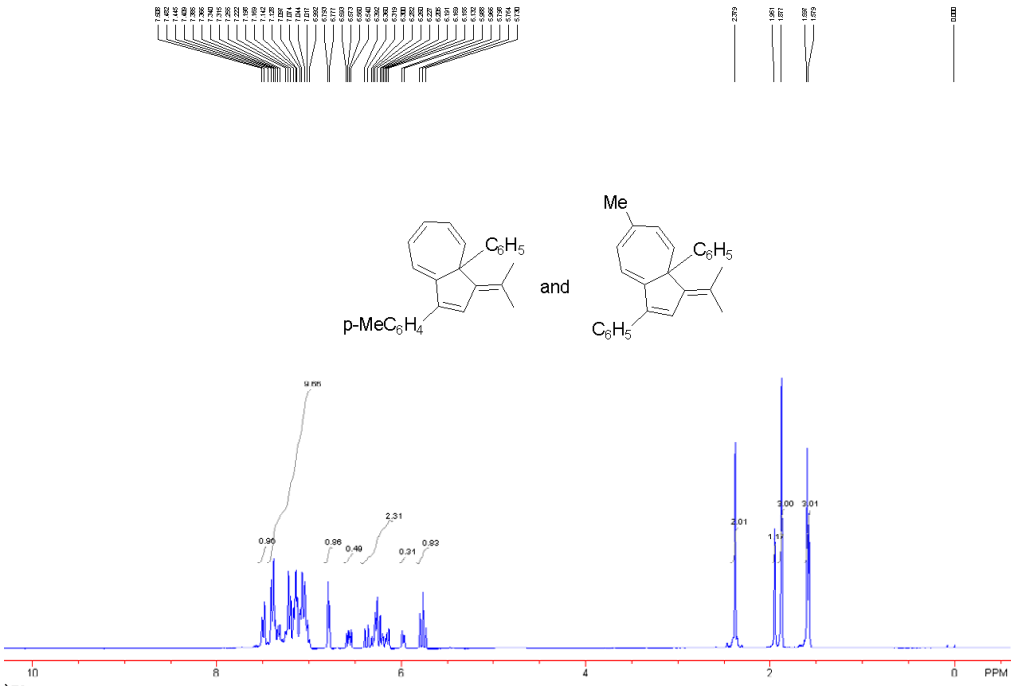


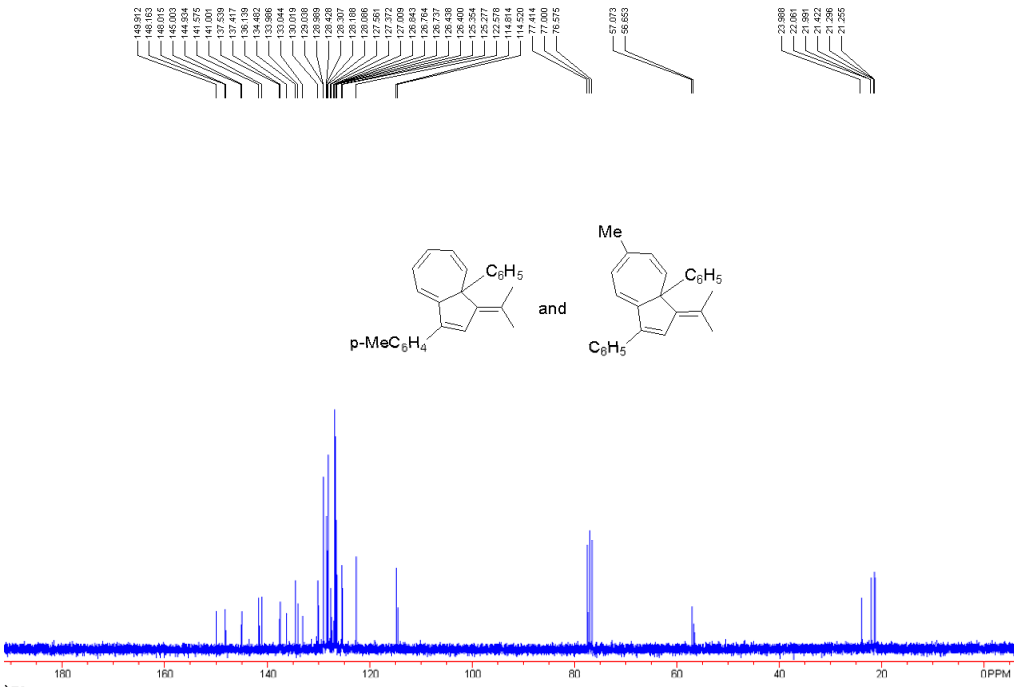


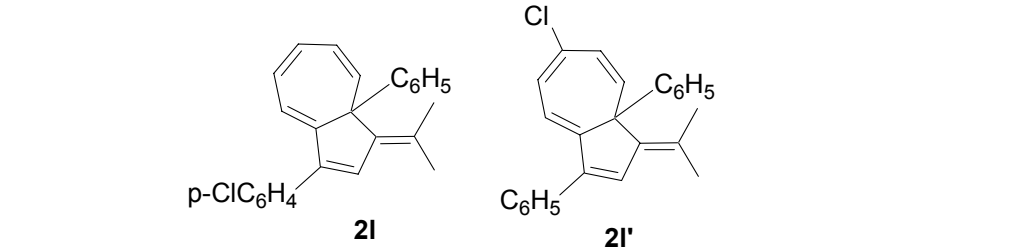
2k **2k'**

A yellow oil. (compound **2k** or **2k'**(1:1.5)) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.58 (s, 3H),

1.88 (s, 3H), 1.95 (s, 3H), 5.75 (d, *J* = 10.2 Hz, 1H), 5.98 (d, *J* = 6.9 Hz, 1H), 6.13-6.39 (m, 2H), 6.78 (s, 1H), 6.99-7.51 (m, 11H). (compound **2k'** or **2k**) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.60 (s, 3H), 1.88 (s, 3H), 2.38 (s, 3H), 5.78 (d, *J* = 9.9 Hz, 1H), 6.13-6.39 (m, 2H), 6.79 (s, 1H), 6.99-7.51 (m, 11H). (compound **2k** or **2k'**) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 22.0, 24.0, 56.7, 114.5, 122.6, 125.3, 126.4, 126.7, 127.0, 127.4, 128.2, 128.4, 129.0, 133.1, 134.0, 136.1, 137.6, 141.0, 145.0, 148.0, 149.9. (compound **2k'** or **2k**) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 21.4, 22.1, 57.1, 114.8, 122.6, 125.4, 126.4, 126.8, 127.0, 127.6, 128.1, 128.3, 129.0, 130.0, 134.5, 136.1, 137.4, 141.6, 144.9, 148.2, 149.9. IR (CH_2Cl_2) ν 3049, 3022, 2923, 2853, 1599, 1491, 1446, 1377, 1179, 1112, 1073, 1029, 876, 820, 757, 702, 510 cm^{-1}. MS (%) m/z 336 (M^+, 100), 321 (62), 259 (34), 306 (31), 229 (26), 337 (24), 291 (24), 215 (20), 243 (17), 289 (12), 202 (10). HRMS (EI) calcd. for $C_{26}H_{24}$: 336.1878, Found: 336.1878.



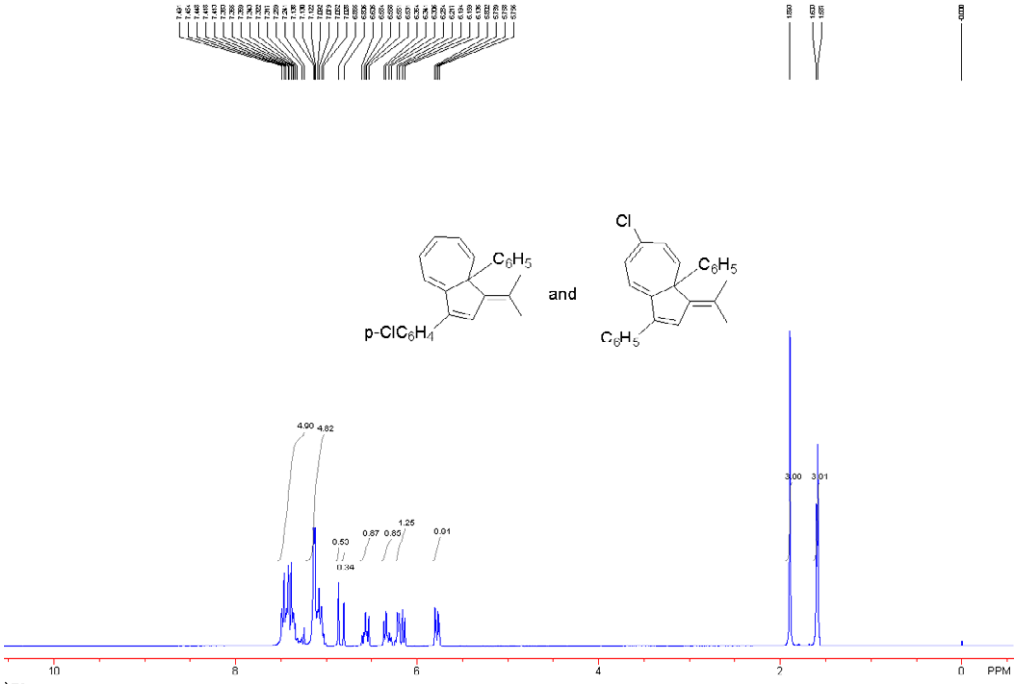


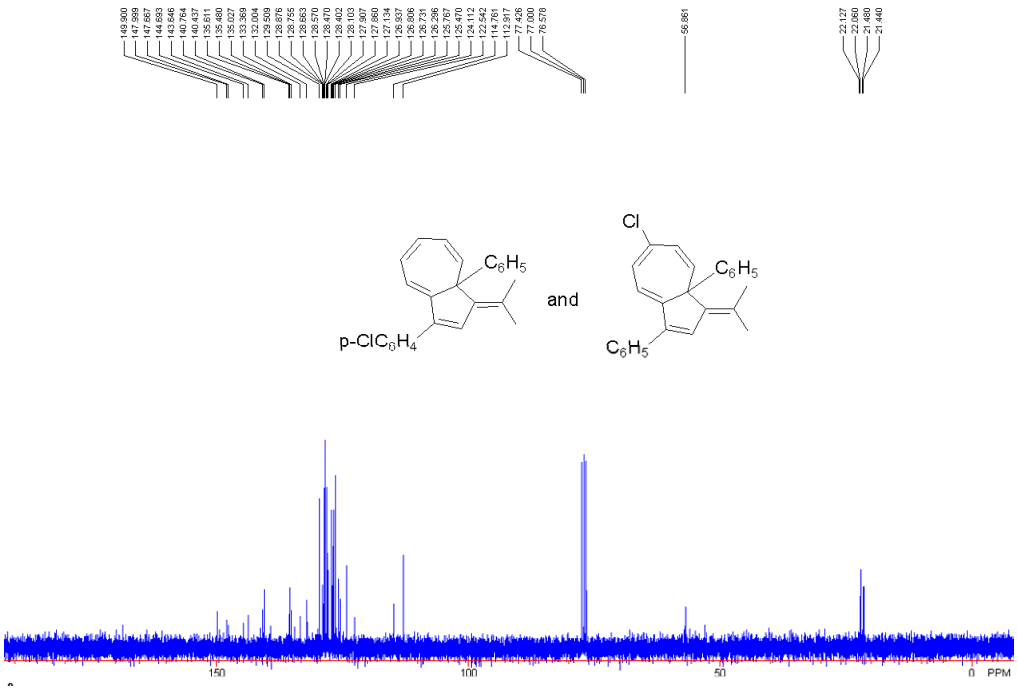


2l **2l'**

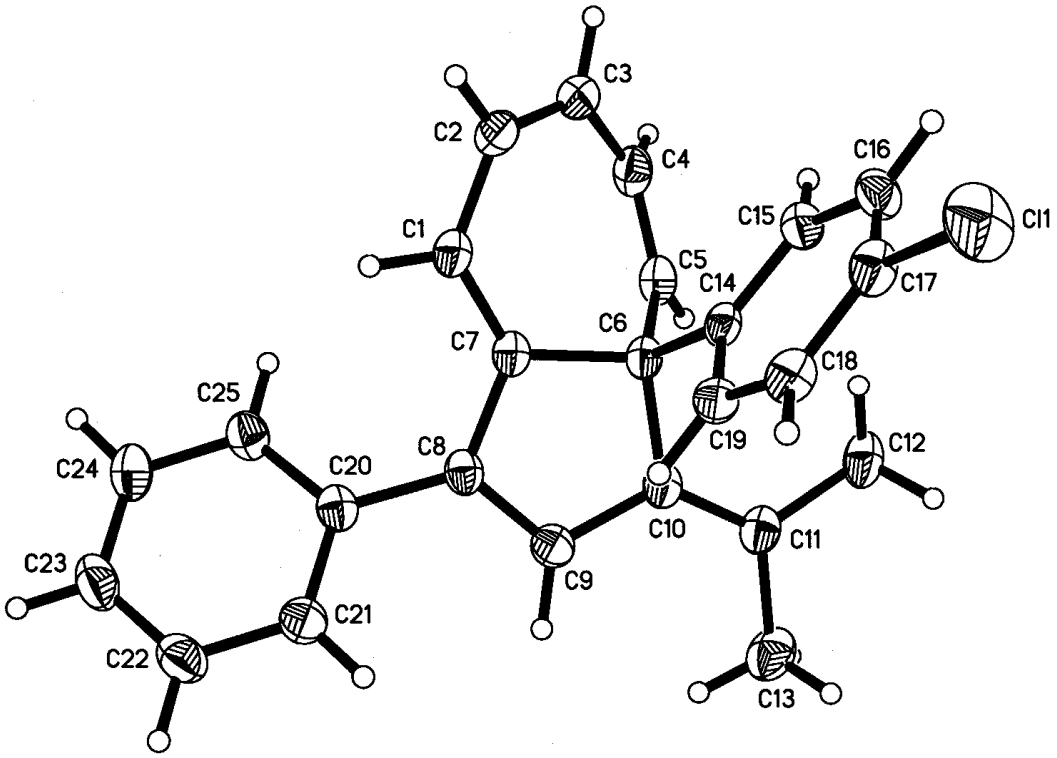
A yellow oil. (compound **2l** or **2l'**(1:1.5)) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.59 (s, 3H), 1.89 (s, 3H), 5.77 (d, *J* = 9.9 Hz, 1H), 6.14-6.22 (m, 1H), 6.29-6.36 (m, 1H), 6.53-6.61 (m, 1H), 6.81 (s, 1H), 7.03-7.14 (m, 5H), 7.24-7.49 (m, 5H). (compound **2l'** or **2l**) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.60 (s, 3H), 1.89 (s, 3H), 5.79 (d, *J* = 10.2 Hz, 1H), 6.14-6.22 (m, 1H), 6.29-6.36 (m, 1H), 6.53-6.61 (m, 1H), 6.87 (s, 1H), 7.03-7.14 (m, 5H), 7.24-7.49 (m, 5H). (compound **2l** or **2l'**) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.4, 22.1, 56.9, 112.9, 122.6, 125.5, 126.3, 126.7, 126.9, 127.9, 128.1, 128.4, 128.6, 128.8, 129.5, 133.4, 135.5, 140.4, 143.7, 147.7, 149.9. (compound **2l'** or **2l**) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.5, 22.1, 56.9, 114.8, 124.1, 125.8, 126.3, 126.8, 127.1, 127.9, 128.1, 128.5, 128.7, 128.9, 132.0, 135.0, 135.6, 140.8, 144.7, 148.0, 149.9. IR (CH_2Cl_2) ν 3057, 3025, 2924, 2852, 1652, 1602, 1487, 1458, 1445, 1372, 1091, 1014, 1003, 832, 758, 701 cm^{-1}. MS (%) m/z 358 (M^++2, 34), 356 (M^+, 100), 279 (71), 291 (54), 341 (46), 306 (38), 358 (34), 229 (31), 278 (25), 314 (26), 215

(23), 276 (21), 202 (11). HRMS (EI) calcd. for $C_{25}H_{21}$: 358.1302, 356.1332, Found: 358.1350, 356.1329.





5. X-ray crystal data of 2d



The crystal data of **2d** have been deposited in CCDC with number 615536. Empirical Formula: $C_{25}H_{21}Cl$; Formula Weight: 356.87; Crystal Color, Habit: colorless, prismatic; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 11.1389(13)Å, b = 13.3200(16)Å, c = 12.4925(15)Å, $\alpha = 90^o$, $\beta = 91.325(2)^o$, $\gamma = 90^o$, V = 1853.0(4)Å^3; Space group: P2(1)/c; Z = 4; D_{calc} = 1.279 g/cm^3; F_{000} = 752; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0442, 0.0896.

Table 1. Crystal data and structure refinement for cd26288.

Identification code	cd26288
Empirical formula	C25 H21 Cl
Formula weight	356.87
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.1389(13) A alpha = 90 deg. b = 13.3200(16) A beta = 91.325(2) deg. c = 12.4925(15) A gamma = 90 deg.
Volume	1853.0(4) A^3
Z, Calculated density	4, 1.279 Mg/m^3
Absorption coefficient	0.211 mm^-1
F(000)	752
Crystal size	0.485 x 0.289 x 0.190 mm
Theta range for data collection	1.83 to 27.00 deg.
Limiting indices	-14<=h<=14, -16<=k<=17, -12<=l<=15
Reflections collected / unique	10735 / 4038 [R(int) = 0.0925]
Completeness to theta = 27.00	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.69317
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4038 / 0 / 289
Goodness-of-fit on F^2	0.821
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.0896
R indices (all data)	R1 = 0.0767, wR2 = 0.0982
Largest diff. peak and hole	0.201 and -0.248 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd26288.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	13707(1)	582(1)	3611(1)	81(1)
C(1)	8394(2)	2662(1)	2144(2)	41(1)
C(2)	9151(2)	2842(2)	1259(2)	49(1)
C(3)	9250(2)	2264(2)	386(2)	53(1)
C(4)	8612(2)	1347(1)	194(2)	49(1)
C(5)	8243(2)	695(1)	921(2)	43(1)
C(6)	8505(1)	753(1)	2109(1)	35(1)
C(7)	7995(1)	1760(1)	2483(1)	36(1)
C(8)	7095(1)	1556(1)	3281(1)	37(1)
C(9)	7003(1)	549(1)	3430(2)	42(1)
C(10)	7779(1)	-11(1)	2743(1)	39(1)
C(11)	7831(1)	-1020(1)	2635(2)	44(1)
C(12)	8584(2)	-1536(1)	1827(2)	56(1)
C(13)	7108(2)	-1722(1)	3304(2)	62(1)
C(14)	9846(1)	684(1)	2447(1)	34(1)
C(15)	10765(2)	584(1)	1740(2)	43(1)
C(16)	11953(2)	539(1)	2101(2)	49(1)
C(17)	12210(1)	599(1)	3170(2)	47(1)
C(18)	11319(2)	683(1)	3905(2)	46(1)
C(19)	10136(2)	725(1)	3533(2)	41(1)
C(20)	6351(1)	2313(1)	3821(1)	39(1)
C(21)	6073(2)	2207(2)	4887(2)	47(1)
C(22)	5342(2)	2888(2)	5390(2)	55(1)
C(23)	4866(2)	3685(2)	4826(2)	59(1)
C(24)	5134(2)	3813(2)	3773(2)	56(1)
C(25)	5873(2)	3140(1)	3269(2)	47(1)

Table 3. Bond lengths [A] and angles [deg] for cd26288.

Cl(1)-C(17)	1.7438(16)
C(1)-C(7)	1.352(2)
C(1)-C(2)	1.426(3)
C(1)-H(1)	0.986(15)
C(2)-C(3)	1.342(3)
C(2)-H(2)	0.922(16)
C(3)-C(4)	1.431(3)
C(3)-H(3)	0.940(19)
C(4)-C(5)	1.328(2)
C(4)-H(4)	0.975(17)
C(5)-C(6)	1.507(2)
C(5)-H(5)	0.937(16)
C(6)-C(10)	1.533(2)
C(6)-C(7)	1.534(2)
C(6)-C(14)	1.545(2)
C(7)-C(8)	1.456(2)
C(8)-C(9)	1.359(2)
C(8)-C(20)	1.477(2)
C(9)-C(10)	1.440(2)
C(9)-H(9)	0.978(17)
C(10)-C(11)	1.351(2)
C(11)-C(12)	1.494(2)
C(11)-C(13)	1.502(2)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.374(2)
C(14)-C(19)	1.388(2)
C(15)-C(16)	1.390(2)
C(15)-H(15)	0.954(16)
C(16)-C(17)	1.363(3)
C(16)-H(16)	0.930(17)
C(17)-C(18)	1.371(3)
C(18)-C(19)	1.389(2)
C(18)-H(18)	0.9300
C(19)-H(19)	0.974(15)
C(20)-C(21)	1.381(2)
C(20)-C(25)	1.399(2)
C(21)-C(22)	1.380(3)
C(21)-H(21)	0.956(16)
C(22)-C(23)	1.374(3)
C(22)-H(22)	0.98(2)
C(23)-C(24)	1.366(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.379(2)
C(24)-H(24)	0.984(17)
C(25)-H(25)	0.954(17)
C(7)-C(1)-C(2)	126.68(18)
C(7)-C(1)-H(1)	114.8(9)
C(2)-C(1)-H(1)	118.5(9)
C(3)-C(2)-C(1)	126.48(19)
C(3)-C(2)-H(2)	120.0(11)
C(1)-C(2)-H(2)	113.2(11)
C(2)-C(3)-C(4)	125.2(2)
C(2)-C(3)-H(3)	119.6(11)
C(4)-C(3)-H(3)	114.8(11)
C(5)-C(4)-C(3)	127.1(2)
C(5)-C(4)-H(4)	118.3(10)
C(3)-C(4)-H(4)	114.5(10)
C(4)-C(5)-C(6)	125.67(17)
C(4)-C(5)-H(5)	120.7(11)
C(6)-C(5)-H(5)	113.6(11)
C(5)-C(6)-C(10)	112.47(13)
C(5)-C(6)-C(7)	106.29(13)

C(10)-C(6)-C(7)	102.65(13)
C(5)-C(6)-C(14)	115.52(14)
C(10)-C(6)-C(14)	109.68(12)
C(7)-C(6)-C(14)	109.34(12)
C(1)-C(7)-C(8)	128.08(15)
C(1)-C(7)-C(6)	123.63(15)
C(8)-C(7)-C(6)	108.20(13)
C(9)-C(8)-C(7)	109.42(15)
C(9)-C(8)-C(20)	124.52(16)
C(7)-C(8)-C(20)	126.02(14)
C(8)-C(9)-C(10)	112.50(16)
C(8)-C(9)-H(9)	124.2(9)
C(10)-C(9)-H(9)	123.2(9)
C(11)-C(10)-C(9)	127.07(16)
C(11)-C(10)-C(6)	125.72(16)
C(9)-C(10)-C(6)	107.15(13)
C(10)-C(11)-C(12)	123.46(16)
C(10)-C(11)-C(13)	122.59(17)
C(12)-C(11)-C(13)	113.94(15)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	118.20(15)
C(15)-C(14)-C(6)	123.97(16)
C(19)-C(14)-C(6)	117.83(15)
C(14)-C(15)-C(16)	120.90(19)
C(14)-C(15)-H(15)	119.3(9)
C(16)-C(15)-H(15)	119.8(9)
C(17)-C(16)-C(15)	119.48(19)
C(17)-C(16)-H(16)	121.4(10)
C(15)-C(16)-H(16)	119.1(10)
C(16)-C(17)-C(18)	121.49(15)
C(16)-C(17)-Cl(1)	119.07(15)
C(18)-C(17)-Cl(1)	119.44(15)
C(17)-C(18)-C(19)	118.37(18)
C(17)-C(18)-H(18)	120.8
C(19)-C(18)-H(18)	120.8
C(14)-C(19)-C(18)	121.54(17)
C(14)-C(19)-H(19)	121.0(8)
C(18)-C(19)-H(19)	117.4(9)
C(21)-C(20)-C(25)	117.68(17)
C(21)-C(20)-C(8)	120.75(16)
C(25)-C(20)-C(8)	121.53(16)
C(22)-C(21)-C(20)	121.33(19)
C(22)-C(21)-H(21)	118.0(10)
C(20)-C(21)-H(21)	120.7(10)
C(23)-C(22)-C(21)	119.9(2)
C(23)-C(22)-H(22)	121.4(12)
C(21)-C(22)-H(22)	118.7(12)
C(24)-C(23)-C(22)	120.0(2)
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	120.3(2)
C(23)-C(24)-H(24)	123.3(11)
C(25)-C(24)-H(24)	116.3(11)
C(24)-C(25)-C(20)	120.7(2)
C(24)-C(25)-H(25)	119.2(10)
C(20)-C(25)-H(25)	120.1(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd26288.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	35(1)	103(1)	105(1)	-2(1)	-17(1)	-2(1)
C(1)	41(1)	33(1)	49(1)	-5(1)	-2(1)	3(1)
C(2)	51(1)	36(1)	62(1)	8(1)	5(1)	2(1)
C(3)	62(1)	45(1)	51(1)	9(1)	12(1)	10(1)
C(4)	58(1)	47(1)	42(1)	-2(1)	-5(1)	16(1)
C(5)	40(1)	40(1)	49(1)	-8(1)	-7(1)	7(1)
C(6)	31(1)	31(1)	44(1)	-3(1)	-1(1)	2(1)
C(7)	32(1)	34(1)	41(1)	-5(1)	-4(1)	2(1)
C(8)	29(1)	38(1)	45(1)	-5(1)	-2(1)	2(1)
C(9)	30(1)	44(1)	53(1)	3(1)	4(1)	-3(1)
C(10)	28(1)	36(1)	51(1)	-3(1)	-3(1)	-1(1)
C(11)	35(1)	35(1)	62(1)	-2(1)	-4(1)	-3(1)
C(12)	53(1)	38(1)	78(2)	-9(1)	-5(1)	6(1)
C(13)	59(1)	41(1)	87(2)	5(1)	1(1)	-8(1)
C(14)	32(1)	25(1)	46(1)	-1(1)	-2(1)	1(1)
C(15)	39(1)	42(1)	47(1)	-2(1)	1(1)	3(1)
C(16)	33(1)	49(1)	65(2)	-2(1)	9(1)	1(1)
C(17)	32(1)	42(1)	67(1)	-1(1)	-10(1)	-2(1)
C(18)	43(1)	43(1)	53(1)	0(1)	-10(1)	-2(1)
C(19)	37(1)	38(1)	47(1)	-1(1)	1(1)	-2(1)
C(20)	28(1)	40(1)	48(1)	-6(1)	-1(1)	-2(1)
C(21)	39(1)	47(1)	55(1)	2(1)	6(1)	-2(1)
C(22)	50(1)	60(1)	57(2)	-6(1)	17(1)	-5(1)
C(23)	47(1)	57(1)	74(2)	-15(1)	16(1)	6(1)
C(24)	50(1)	51(1)	68(2)	-5(1)	-2(1)	15(1)
C(25)	45(1)	51(1)	45(1)	-4(1)	0(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd26288.

	x	y	z	U(eq)
H(12A)	8076	-1802	1265	85
H(12B)	9024	-2073	2166	85
H(12C)	9137	-1064	1531	85
H(13A)	6578	-1341	3743	93
H(13B)	7639	-2115	3753	93
H(13C)	6645	-2160	2845	93
H(18)	11503	710	4634	56
H(23)	4361	4137	5160	71
H(1)	8133(12)	3239(11)	2573(12)	39(4)
H(2)	9532(14)	3456(13)	1294(14)	54(5)
H(3)	9698(16)	2494(13)	-193(15)	59(6)
H(4)	8411(14)	1216(12)	-557(15)	55(5)
H(5)	7755(14)	150(12)	721(14)	50(5)
H(9)	6445(14)	232(12)	3919(14)	48(5)
H(15)	10579(13)	531(11)	992(14)	39(5)
H(16)	12558(14)	491(11)	1603(14)	44(5)
H(19)	9514(13)	798(10)	4063(12)	34(4)
H(21)	6379(13)	1654(12)	5298(13)	45(5)
H(22)	5191(17)	2799(14)	6156(17)	73(6)
H(24)	4818(15)	4369(13)	3332(15)	58(5)
H(25)	6057(14)	3244(12)	2536(14)	46(5)

Table 6. Torsion angles [deg] for cd26288.

C(7)-C(1)-C(2)-C(3)	26.7(3)
C(1)-C(2)-C(3)-C(4)	-0.6(3)
C(2)-C(3)-C(4)-C(5)	-30.5(3)
C(3)-C(4)-C(5)-C(6)	-4.9(3)
C(4)-C(5)-C(6)-C(10)	170.44(15)
C(4)-C(5)-C(6)-C(7)	58.9(2)
C(4)-C(5)-C(6)-C(14)	-62.6(2)
C(2)-C(1)-C(7)-C(8)	-170.59(16)
C(2)-C(1)-C(7)-C(6)	13.2(3)
C(5)-C(6)-C(7)-C(1)	-63.20(18)
C(10)-C(6)-C(7)-C(1)	178.53(14)
C(14)-C(6)-C(7)-C(1)	62.1(2)
C(5)-C(6)-C(7)-C(8)	119.97(14)
C(10)-C(6)-C(7)-C(8)	1.70(15)
C(14)-C(6)-C(7)-C(8)	-114.70(14)
C(1)-C(7)-C(8)-C(9)	-176.68(15)
C(6)-C(7)-C(8)-C(9)	-0.04(17)
C(1)-C(7)-C(8)-C(20)	5.7(3)
C(6)-C(7)-C(8)-C(20)	-177.67(13)
C(7)-C(8)-C(9)-C(10)	-1.84(19)
C(20)-C(8)-C(9)-C(10)	175.83(14)
C(8)-C(9)-C(10)-C(11)	-174.38(15)
C(8)-C(9)-C(10)-C(6)	2.94(18)
C(5)-C(6)-C(10)-C(11)	60.85(19)
C(7)-C(6)-C(10)-C(11)	174.68(15)
C(14)-C(6)-C(10)-C(11)	-69.17(19)
C(5)-C(6)-C(10)-C(9)	-116.52(14)
C(7)-C(6)-C(10)-C(9)	-2.69(15)
C(14)-C(6)-C(10)-C(9)	113.46(14)
C(9)-C(10)-C(11)-C(12)	174.06(15)
C(6)-C(10)-C(11)-C(12)	-2.8(2)
C(9)-C(10)-C(11)-C(13)	-4.5(3)
C(6)-C(10)-C(11)-C(13)	178.68(14)
C(5)-C(6)-C(14)-C(15)	0.5(2)
C(10)-C(6)-C(14)-C(15)	128.88(16)
C(7)-C(6)-C(14)-C(15)	-119.28(17)
C(5)-C(6)-C(14)-C(19)	-179.44(14)
C(10)-C(6)-C(14)-C(19)	-51.08(18)
C(7)-C(6)-C(14)-C(19)	60.76(18)
C(19)-C(14)-C(15)-C(16)	-0.8(2)
C(6)-C(14)-C(15)-C(16)	179.22(14)
C(14)-C(15)-C(16)-C(17)	-0.4(3)
C(15)-C(16)-C(17)-C(18)	1.4(3)
C(15)-C(16)-C(17)-Cl(1)	-177.95(13)
C(16)-C(17)-C(18)-C(19)	-1.3(3)
Cl(1)-C(17)-C(18)-C(19)	178.11(12)
C(15)-C(14)-C(19)-C(18)	1.0(2)
C(6)-C(14)-C(19)-C(18)	-179.05(14)
C(17)-C(18)-C(19)-C(14)	0.0(2)
C(9)-C(8)-C(20)-C(21)	40.1(2)
C(7)-C(8)-C(20)-C(21)	-142.56(16)
C(9)-C(8)-C(20)-C(25)	-137.76(17)
C(7)-C(8)-C(20)-C(25)	39.5(2)
C(25)-C(20)-C(21)-C(22)	0.4(2)
C(8)-C(20)-C(21)-C(22)	-177.55(15)
C(20)-C(21)-C(22)-C(23)	0.7(3)
C(21)-C(22)-C(23)-C(24)	-1.3(3)
C(22)-C(23)-C(24)-C(25)	0.6(3)
C(23)-C(24)-C(25)-C(20)	0.6(3)
C(21)-C(20)-C(25)-C(24)	-1.1(2)
C(8)-C(20)-C(25)-C(24)	176.88(16)

Symmetry transformations used to generate equivalent atoms:

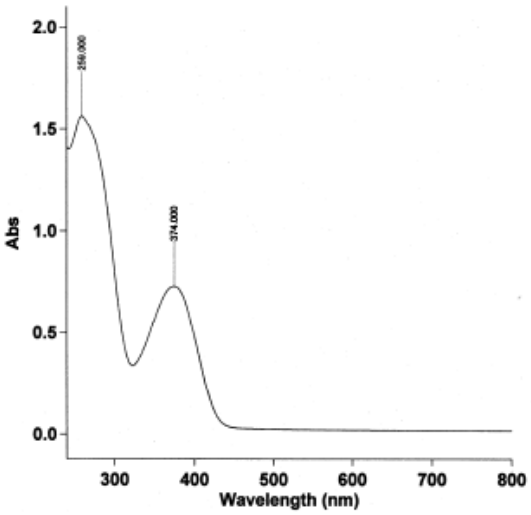
Table 7. Hydrogen bonds for cd26288 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

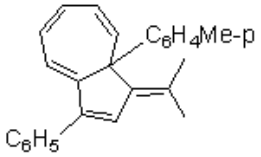
6. UV absorption spectra of products **2b**, **2c**, **2d**.

2007-11-19 10:46:43 Page 1 of 1

Varian cary 500 UV-Vis-NIR Spectrophotometer



Scan Analysis Report



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Operator:

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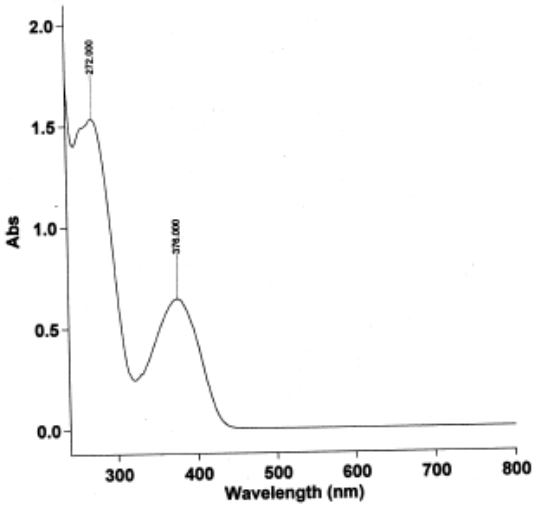
Collection Time 2007-11-19 10:31:11

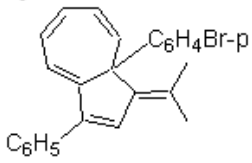
Peak Table
Peak Style Peaks
Peak Threshold 0.01000
Range 800.000nm to 240.000nm

Wavelength (nm)	Abs
374.000	0.72642
259.000	1.56161

2007-11-19 10:46:09 Page 1 of 1

Varian cary 500 UV-Vis-NIR Spectrophotometer





2b

Scan Analysis Report

Report Time : 星期一 19 十一月 10:45:42 AM 2007
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Operator:

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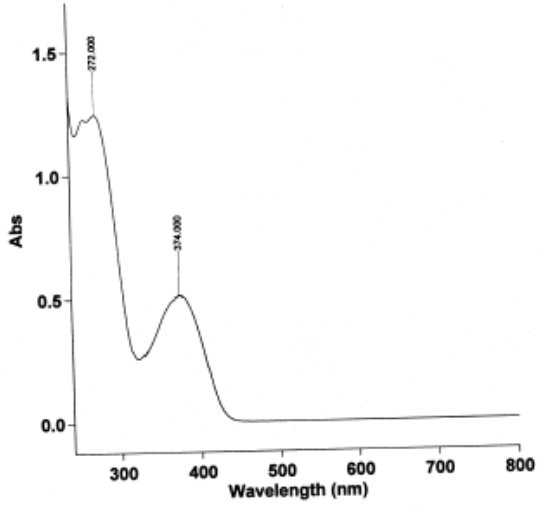
Collection Time 2007-11-19 10:34:59

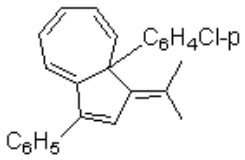
Peak Table
Peak Style Peaks
Peak Threshold 0.01000
Range 800.000nm to 240.000nm

Wavelength (nm)	Abs
376.000	0.64180
272.000	1.53521

2007-11-19 10:45:25 Page 1 of 1

Varian cary 500 UV-Vis-NIR Spectrophotometer





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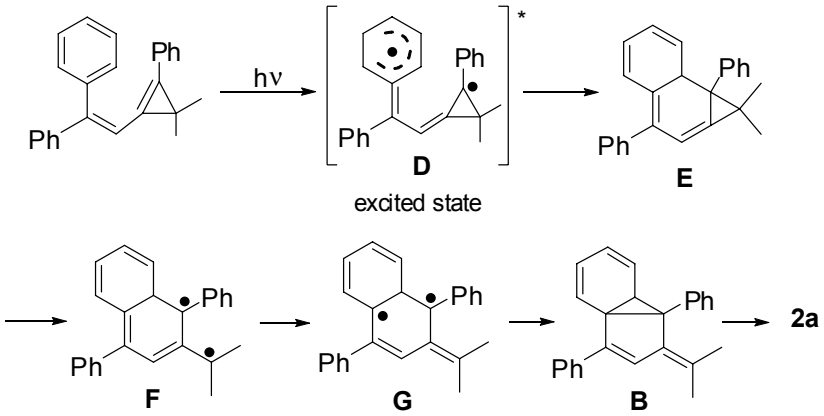
Software version: 02.00(25)
Operator:
Sample Name: yf-2-8 07-1258
Collection Time 2007-11-19 10:38:52

Peak Table
Peak Style Peaks
Peak Threshold 0.01000
Range 800.000nm to 240.000nm

Wavelength (nm)	Abs
374.000	0.51256
272.000	1.24539

Another explanation to account for the formation of **2** is outlined in the Supporting Information (Scheme 2), photo-induced pericyclic reaction gives intermediate **E** via intermediate **D** (excited state),[10] which produces biradical intermediate **F**.[11] 1,5-Migration of **F** gives biradical intermediate **G**, which provides **2a** via intermediate **B**. However, this longer reaction pathway involved biradical intermediates **F** and **G**, which should be influenced by molecular oxygen during photo-irradiation, rendering that this process is impossible to involve the formation of **2a**.



Scheme 2. A Plausible Reaction Mechanism via Pericyclic Reaction

10. The formation of **E** can also be considered through intermediate **D**.
11. X. Creary, M. E. Mehrsheikh-Mohammadi, S. McDonald, *J. Org. Chem.* **1987**, *52*, 3254-3263.

7. **Reference**

[1] Shao, L.-X.; Zhang; Y.-P.; Qi, M.-H.; Shi, M. *Org. Lett.* **2007**, *9*, 117.