

# New Aryl-Substituted Norbornadienes with Red-Shifted Absorption for Molecular Solar Thermal Energy Storage

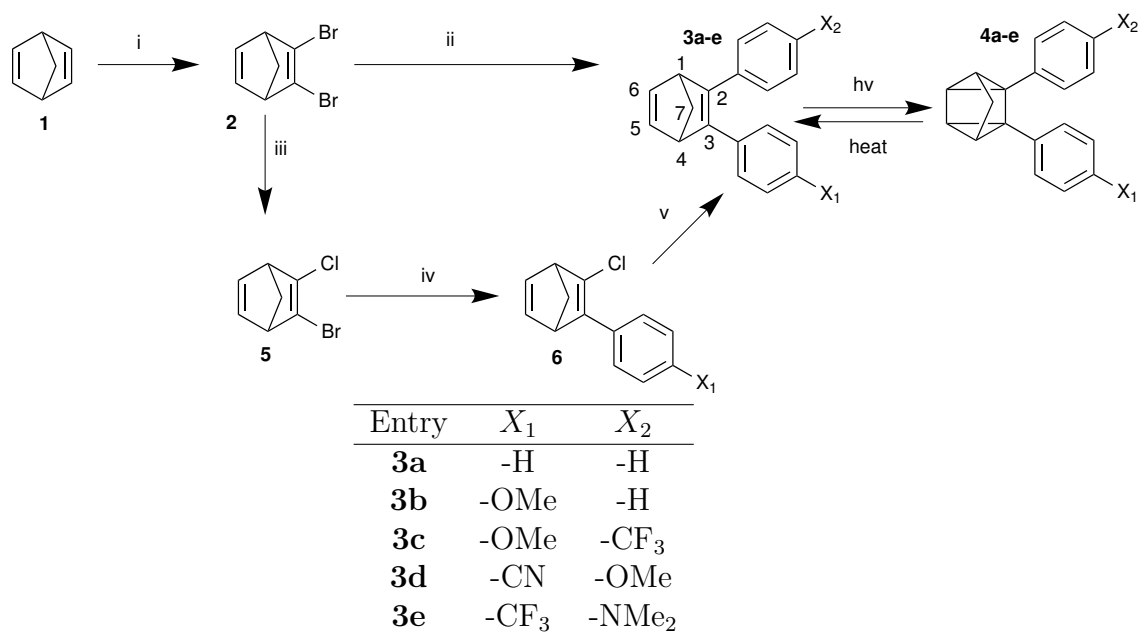
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## Supporting Information

### Experimental procedure

Reagents were purchased from Sigma Aldrich, Acros Organics or Fischer Scientific and were used without further purification if not stated otherwise. Dry THF was obtained from a MB SPS-800 solvent drying system from MBRAUN and was degassed before usage. Glassware was dried at 120°C for a minimum of 3 h, in an DRY-Line oven from VWR. NMR analysis was made using a 400 MHz Varian 400-MR. An overview of the synthetic routes are shown in figure S1. ESI-FTMS was performed at Proteomics Core Facility, Sahlgrenska Academy at University of Gothenburg. UV/VIS absorption spectra were recorded on a Cary 4000 spectrophotometer. IR analysis was run on a Perkin Elmer system 2000 FTIR with KBr pellets. Compounds dibromo-norbornadiene (**2**) and 2-chloro-3-bromo-norbornadiene were synthesized according to published procedures.<sup>1</sup> Synthesized norbornadienes **3a-e** were soluble in acetonitrile, chloroform, DMSO and toluene. However, for practical reasons, only toluene was used for UV/VIS characterization and the kinetic studies.



**Figure S1:** Synthesis of aryl-substituted norbornadienes. i) a) THF, *t*-BuOK, *n*-BuLi 2 h, -70°C to -40°C b) 1,2-dibromoethane (0.5 equiv.), 1.5 h, -40°C, c) 1,2-dibromoethane (1.5 equiv.), 2 h, -40°C, room temp. 4 h. ii) THF, Pd<sub>2</sub>(dba)<sub>3</sub> (2-5 mol%), *t*-Bu<sub>3</sub>P (7-14 mol%), CsF, phenylboronic acid, 24 h, room temp. iii) THF, -78°C, *t*-BuLi, 30 min, TsCl, 45 min, room temp. 1 h. iv) THF, Pd<sub>2</sub>(dba)<sub>3</sub> (2-5 mol%), *t*-Bu<sub>3</sub>P (7-14 mol%), CsF, arylboronic acid, 24 h, room temp. v) THF, Pd<sub>2</sub>(dba)<sub>3</sub> (2-5 mol%), *t*-Bu<sub>3</sub>P (7-14 mol%), CsF, arylboronic acid, 48 h, 65°C. Quadricyclanes **4a-e** were obtained by irradiating corresponding norbornadiene.

### 2-Chloro-3-(4-Methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (**6b/c**)

**6b/c** was synthesized according to previous published procedures<sup>2</sup> with minor modifications. To a dried Schlenk tube [Pd<sub>2</sub>(dba)<sub>3</sub>] (123.2 mg, 0.13 mmol, 2.5 mol%), 4-methoxyphenylboronic acid (756.3 mg, 5.0 mmol), CsF (2.682 g, 17.7 mmol) and **5** (1.119 g, 5.4 mmol) was added under nitrogen. Dry THF (5.8 ml) was added followed by tri-*tert*-butylphosphine (380 μl, 1 M) and the reaction was stirred at 25°C for 24 h. The crude product was first filtered and then purified by column chromatography (EtOAc-Hexanes, 0:1, 1:49) to give **6b/c** (706.1 mg, 3.0 mmol, 60.1%, hexane content: 15.2%, by NMR) as of white crystals. R<sub>f</sub>=0.37 (EtOAc-Hexanes, 5:95) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.59 – 7.52 (m, 2H), 6.95 – 6.89 (m, 4H), 3.95 (m, 1H), 3.56 (m, 1H), 2.33 (dt, J = 6.2, 1.6 Hz, 1H), 2.11 ppm (dt, J = 6.2, 1.8 Hz, 1H). Spectroscopic data are in good agreement with those reported previously<sup>2</sup>

### 2-Chloro-3-(4-cyanophenyl)bicyclo[2.2.1]hepta-2,5-diene (**6d**)

To a dried Schlenk tube [Pd<sub>2</sub>(dba)<sub>3</sub>] (227.7 mg, 0.24 mmol, 2.5 mol%), 4-cyanophenylboronic acid (1138.9 mg, 7.8 mmol), CsF (4913.5 g, 32.3 mmol) and **5** (2.20 g, 10.7 mmol) was added under nitrogen. Dry THF (7.6 ml) was added followed by tri-*tert*-butylphosphine (0.68 ml, 1 M) and the reaction was stirred at 25°C for 48 h. The crude product was first filtered and then purified by column chromatography (EtOAc-Hexanes, 0:1, 1:9) to give **6d** (148.1 mg, 0.65 mmol, 8.3 %) as a pale oil. R<sub>f</sub>=0.39 (EtOAc-Hexanes, 1:9). IR:  $\tilde{\nu}$  = 3801 (w), 3751 (w), 3735 (w), 3649 (w), 1700 (w), 1684 (w), 1652 (w), 1560 (w), 1507 (w), 1275 (m), 1268 (m), 763 (s), 750 (s), 668 (m), 457 (w), 445 (w), 433 (w), 426 (w), 418 (s) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.71 – 7.59 (m, 4H), 6.95 (m, 2H), 3.95 (m, 1H), 3.62 (m, 1H), 2.36 (dq, J = 6.7, 1.6 Hz, 1H), 2.18 ppm (dq, J = 6.6, 1.6 Hz, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 400 MHz): δ 145.8 (C3), 143.1 (Ar), 141.7 (C6), 141.5 (C5), 138.7 (C2), 133.4 (Ar), 132.6 (Ar), 132.0 (Ar), 126.3 (Ar), 119.0 (CN), 110.2 (Ar-CN), 69.8 (C7), 59.0 (C1), 53.6 (C4) ppm.

### 2-Chloro-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hepta-2,5-diene (**6e**)

To a dried Schlenk tube [Pd<sub>2</sub>(dba)<sub>3</sub>] (58 mg, 0.06 mmol, 5 mol%), 4-trifluoromethylphenylboronic acid (231.8 mg, 1.20 mmol), CsF (644.5 mg, 4.24 mmol)

and **5** (237.1 g, 1.15 mmol) was added under nitrogen. Dry THF (0.8 ml) was added followed by tri-*tert*-butylphosphine (180  $\mu$ l, 1 M) and the reaction was stirred at 25°C for 24 h. The crude product was first filtered and then purified by column chromatography (Hexanes) to give **6e** (78 mg, 0.29 mmol, 25%) as a clear oil.  $R_f$  = 0.44 (Hexanes). IR:  $\tilde{\nu}$  = 3647 (w), 2992 (m), 2943 (m), 2874 (w), 1684 (w), 1653 (w), 1616 (m), 1559 (w), 1540 (w), 1410 (m), 1327 (s), 1301 (m), 1291 (m), 1252 (m), 1167 (s), 1122 (s), 1069 (s), 1055 (m), 1015 (m), 885 (w), 840 (w), 807 (w), 789 (w), 764 (w), 717 (m), 655 (w), 600 (m), 519 (m), 489 (w), 472 (w)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.71 – 7.66 (m, 2H), 7.64 – 7.59 (m, 2H), 6.99 – 6.94 (m, 2H), 3.96 (m, 1H), 3.61 (m, 1H), 2.37 (dt,  $J$  = 6.4, 1.7 Hz, 1H), 2.18 ppm (dt,  $J$  = 6.4, 1.8 Hz, 1H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  144.2 (C3), 143.4 (C5), 141.7 (Ar), 141.6 (C6), 137.8 (C2), 128.9 (Ar), 128.6 (Ar- $\text{CF}_3$ ), 127.6 (Ar), 126.1 (Ar), 125.2 ( $\text{CF}_3$ ), 122.8 (Ar), 69.9 (C7), 58.8 (C1), 53.8 (C4), 31.60 ppm.  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  -62.58 ppm.

### 2,3-diphenylbicyclo[2.2.1]hepta-2,5-diene (**3a**)

**3a** was synthesized according to previous published procedures<sup>2</sup> with minor modifications. To a dried Schlenk tube [ $\text{Pd}_2(\text{dba})_3$ ] (91.1 mg, 0.1 mmol, 5 mol%), phenylboronic acid (541.5 mg, 4.4 mmol), CsF (2.136 g, 14.1 mmol) and dibromide **2** (516.2 mg, 2.1 mmol) was added under nitrogen. Dry THF (2.7 ml) was added followed by tri-*tert*-butylphosphine (270  $\mu$ l, 1 M) and the reaction was kept at 25°C for 24 h. The crude product was first filtered and then purified by column chromatography (hexanes) to give **3a** (114.1 mg, 0.5 mmol, 23.4%) as a white solid.  $R_f$  = 0.14. IR:  $\tilde{\nu}$  = 3648 (m, br), 2988 (s), 2869 (s), 1492 (w), 1442 (w), 1384 (w), 1296 (w), 1142 (s), 1077 (w), 755 (m), 720 (w), 694 (m), 666 (w), 468 (w), 412 (w)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.24 (m, 8H), 7.20 (m, 2H), 7.00 (t, 2H,  $J$  = 1.9 Hz), 3.90 (m, 2H), 2.39 (dt, 1H,  $J$  = 6.2, 1.7 Hz), 2.10 (dt, 1H,  $J$  = 6.2, 1.6 Hz).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.28 – 7.22 (m, 4H), 7.20 – 7.15 (m, 6H), 7.02 (t,  $J$  = 1.9 Hz, 2H), 3.87 (m, 2H), 2.26 (dt,  $J$  = 6.2, 1.7 Hz, 1H), 1.98 ppm (dt,  $J$  = 6.2, 1.6 Hz, 1H). Spectroscopic data are in good agreement with those reported previously<sup>2</sup>. FTMS(ESI) calcd ( $\text{C}_{19}\text{H}_{16}$ ): 244.1242 found: 244.1252 ( $[\text{M}]^+$ , 31%), 261.1263 ( $[\text{M}+\text{OH}]^+$ , 94), 277.1217 ( $[\text{M}+\text{H}+2\text{O}]^+$ , 100), 293.1167 ( $[\text{M}+\text{H}+3\text{O}]^+$ , 50).

### Asymmetric Aryl-substituted-Norbornadiene (**3b-e**), general procedure

Procedures followed those previously published,<sup>2</sup> with modifications. To a dried Schlenk tube, [ $\text{Pd}_2(\text{dba})_3$ ] (20-60 mg, 2.5 mol%) was added together

with CsF (0.5-8.2 mmol, 3.3 equiv.) and arylboronic acid (0.9-3.0 mmol, 1.1 equiv.). Under inert atmosphere ( $N_2$ ), 2-chloro-3-(4-aryl)-norbornadiene, **6b-e**, was added (0.8-1.3 mmol) and the mixture was dissolved in THF (1.6-2.5 ml) at 65°C. Tri-*tert*-butylphosphine (60-90  $\mu$ l, 7 mol%) was added and the mixture was stirred at 65°C for 48 h. The crude product was filtered and then purified by column chromatography.

### 2-(4-methoxyphenyl)-3-phenylbicyclo[2.2.1]hepta-2,5-diene (**3b**)

Preparations followed the procedure described above with phenylboronic acid (173.3 mg, 1.4 mmol), norbornadiene **6b** (302.2 mg, 1.3 mmol) and THF (2.5 ml). Purification was done by column chromatography (EtOAc-Hexanes, 0:1, 1:49) to give **3b** (208.4 mg, 0.76 mmol, 58.5%) as a clear oil. IR:  $\tilde{\nu}$  = 3464 (w,br), 3060 (w), 2966 (m), 2931 (m), 2864 (w), 2834 (w), 1605 (m), 1571 (w), 1557 (w), 1508 (s), 1489 (w), 1462 (w), 1441 (w), 1289 (m), 1246 (s), 1174 (m), 1118 (w), 1037 (m), 883 (w), 832 (m), 812 (w), 794 (w), 777 (w), 761 (w), 729 (w), 717 (w), 697 (m), 677 (w), 660 (w), 610 (w), 582 (w), 553 (w), 505 (w), 478 (w), 468 (w), 442 (w), 425 (w), 418 (w)  $cm^{-1}$ .  $^1H$ -NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.49 (d, 2H,  $J=8.1$  Hz), 7.34 (d, 2H,  $J=8.7$  Hz), 7.24 (m, 4H), 7.18 (m, 3H), 6.96 (m, 2H), 6.79 (dm, 2H,  $J=8.9$  Hz), 3.86 (m, 2H), 3.79 (s, 3H), 2.34 (dt, 1H,  $J=6.1, 1.6$  Hz), 2.07 ppm (dt, 1H,  $J=6.1, 1.6$  Hz).  $^1H$ -NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  7.27 – 7.22 (m, 2H), 7.20 – 7.15 (m, 3H), 7.14 – 7.09 (m, 2H), 6.99 (m, 2H), 6.85 – 6.79 (m, 2H), 3.84 (m, 2H), 3.71 (s, 3H), 2.22 (dt,  $J = 6.1, 1.6$  Hz, 1H), 1.95 ppm (dt,  $J = 6.2, 1.7$  Hz, 1H). Spectroscopic data are in good agreement with those reported previously<sup>2</sup>. FTMS(ESI) calcd( $C_{20}H_{18}O$ ): 274.1358, found: 275.1418 ( $[MH]^+$ , 100%), 291.1376 ( $[M+O]^+$ , 54), 307.1330 ( $[M+2O]^+$ , 28).

### 2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hepta-2,5-diene (**3c**)

Preparations followed the procedure described above with 4-(Trifluoromethyl)-phenylboronic acid (181.2 mg, 0.95 mmol), norbornadiene **6c** (199.5 mg, 0.86 mmol) and THF (1.6 ml). Purification was done by column chromatography (EtOAc-Hexanes, 0:1, 5:95) to give **3c** (215.2 mg, 0.63 mmol, 73.3%) as a clear, light yellow oil.  $R_f=0.46$  (EtOAc- Hexanes, 5:95). IR:  $\tilde{\nu}$  = 3435 (m,br), 2970 (w), 1613 (m), 1515 (w), 1505 (m), 1463 (w), 1409 (w), 1324 (s), 1290 (w), 1249 (m), 1164 (m), 1121 (m), 1067 (m), 1015 (w), 832 (m), 797 (w), 717 (w), 597 (w), 517 (w), 472 (w), 464 (w), 438 (w), 420 (m),

409 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.49 (d, 2H,  $J=8.1$  Hz), 7.34 (d, 2H,  $J=8.7$  Hz), 7.16 (dm, 2H,  $J=8.9$  Hz), 6.98 (m, 2H), 3.88 (m, 2H), 3.80 (s, 3H), 2.36 (dt, 1H,  $J=4.6, 1.5$  Hz), 2.10 ppm (dt, 1H,  $J=4.6, 1.6$  Hz).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.63 – 7.57 (m, 2H), 7.38 (dp,  $J = 7.7, 0.9$  Hz, 2H), 7.16 – 7.09 (m, 2H), 7.01 (dddd,  $J = 14.3, 5.2, 2.8, 0.9$  Hz, 2H), 6.88 – 6.83 (m, 2H), 3.88 (dtq,  $J = 6.9, 2.6, 1.3$  Hz, 2H), 3.72 (s, 3H), 2.25 (dt,  $J = 6.2, 1.6$  Hz, 1H), 1.98 ppm (dt,  $J = 6.3, 1.6$  Hz, 1H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  158.8 (ArC-OMe), 151.0 (C2), 145.5 (C3), 142.4 (C5 and C6), 141.6 (ArC), 129.6 (ArC), 128.2 (Ar- $\text{CF}_3$ ), 127.1 (ArC), 125.1 ( $\text{CF}_3$ ), 113.9 (ArC), 70.2 (C7), 57.0 (C1), 56.4 (C4), 55.2 ppm ( $\text{CH}_3$ ).  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  -62.42.  $^{19}\text{F-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -60.84 ppm. FTMS(ESI) calcd( $\text{C}_{21}\text{H}_{17}\text{F}_3\text{O}$ ): 342.1231, found: 342.1221 ( $[\text{M}]^+$ , 18%), 359.1244 ( $[\text{M}+\text{OH}]^+$ , 100) 375.1195 ( $[\text{M}+\text{H}+2\text{O}]$ , 33).

#### 4-(3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)-benzonitrile (3d)

Preparations followed the procedure described above with  $[\text{Pd}_2(\text{dba})_3]$  (30 mg, 5 mol%) 4-(methoxy)phenylboronic acid (111.15 mg, 0.73 mmol), norbornadiene **6d** (147.6 mg, 0.65 mmol) and THF (1.25 ml). Purification was done on a Biotage Flash Purification System with a 10 g silica column and EtOAc, 2%-20%, in Heptane to yield **3d** (32.2 mg, 0.11 mmol, 16.5%) as a clear, light yellow oil.  $R_f=0.32$  (EtOAc-Hexanes, 1:9). IR:  $\tilde{\nu} = 3636$  (s,br), 2964 (s), 2326 (w), 2223 (m), 1600 (s), 1510 (s), 1292 (m), 1259 (s), 1173 (m), 1091 (s), 1024 (s), 799 (s), 716 (w), 666 (w), 578 (w), 554 (w), 490 (w), 477 (w), 449 (w), 432 (w), 423 (w), 417 (w)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52 – 7.45 (m, 2H), 7.33 – 7.28 (m, 2H), 7.14 – 7.09 (m, 2H), 6.99 – 6.93 (m, 2H), 6.84 – 6.78 (m, 2H), 3.87 (dt,  $J = 3.9, 1.6$  Hz, 2H), 3.80 (s, 3H), 2.34 (dt,  $J = 6.3, 1.7$  Hz, 1H), 2.10 ppm (dt,  $J = 6.3, 1.6$  Hz, 1H).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.72 – 7.67 (m, 2H), 7.38 – 7.33 (m, 2H), 7.14 – 7.08 (m, 2H), 7.04 – 6.95 (m, 2H), 6.89 – 6.83 (m, 2H), 3.93 – 3.85 (m, 2H), 3.73 (s, 3H), 2.24 (dt,  $J = 6.2, 1.6$  Hz, 1H), 1.98 ppm (dt,  $J = 6.3, 1.6$  Hz, 1H).  $^{13}\text{C-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.0 (ArC-OMe), 152.7 (C2), 145.2 (C3), 142.6 (ArC), 142.4 (C5 and C6), 132.0 (ArCH), 129.4 (ArCH), 128.3 (ArC), 127.4 (ArCH), 119.2 (CN), 114.1 (ArCH), 114.0 (ArC-CN), 70.2 (C7), 57.3 (C1), 56.1 (C4), 55.2 ppm ( $\text{CH}_3$ ). FTMS(ESI) calcd( $\text{C}_{21}\text{H}_{17}\text{NO}$ ): 299.1310, found: 300.1380 ( $[\text{MH}]^+$ , 100%).

### **N,N-dimethyl-4-(3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)aniline (3e)**

Preparations followed the procedure described above with [Pd<sub>2</sub>(dba)<sub>3</sub>] (7.7 mg, 5 mol%), 4-(dimethylamino)phenylboronic acid (31.2 mg, 0.19 mmol), norbornadiene **6e** (44.7 mg, 0.165 mmol) and THF (0.32 ml). Purification was done by column chromatography (EtOAc-Hexanes, 0:1, 1:9) to give **3e** (22.8 mg, 0.06 mmol, 39%) as a clear, yellow oil.  $R_f=0.37$  (EtOAc-Hexanes, 1:9). IR:  $\tilde{\nu} = 3499$  (s,b), 2977 (m), 2869 (m), 1661 (m), 1608 (m), 1523 (m), 1384 (m), 1352 (w), 1324 (s), 1163 (m), 1123 (s), 1067 (m), 1016 (w), 928 (w), 818 (w), 714 (w), 558 (w), 482 (w), 464 (w), 442 (w), 428 (w), 416 (w), 406 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.18 – 7.08 (m, 2H), 7.00 – 6.91 (m, 2H), 6.65 – 6.60 (m, 2H), 3.89 (m, 1H), 3.84 (m, 1H), 2.95 (s, 6H), 2.32 (dt, J = 6.2, 1.7 Hz, 1H), 2.06 ppm (dt, J = 6.2, 1.6 Hz, 1H). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.58 (d, J = 7.7 Hz, 2H), 7.41 (d, J = 7.7, 0.9 Hz, 2H), 7.06 (m, 2H), 6.97 (m, 2H), 6.65 – 6.58 (m, 2H), 3.86 (m, 2H), 2.87 (s, 6H), 2.21 (dt, J = 6.2, 1.7 Hz, 1H), 1.95 ppm (dt, J = 6.2, 1.6 Hz, 1H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  151.4 (ArC-N), 149.6 (C2), 143.5 (C3), 142.4 (C5 and C6), 142.1 (ArC), 128.0 (ArC-CF<sub>3</sub>), 127.1 (ArCH and ArC), 125.0 (ArCH and CF<sub>3</sub>), 112.1 (ArCH), 69.8 (C7), 56.7 (C1), 56.4 (C4), 40.3 ppm (N(CH<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  -62.35 ppm. <sup>19</sup>F-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  -60.78 ppm. FTMS(ESI) calcd(C<sub>22</sub>H<sub>20</sub>F<sub>3</sub>N): 355.1548, found: 356.1619 ([MH]<sup>+</sup>, 22%), 388.1510 ([M+2O]<sup>+</sup>, 100), 406.1611 ([M+2H+3O]<sup>+</sup>, 38).

### **1,5-diphenyltetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane (4a)**

**4a** was obtained from **3a** after irradiation by a Osram Powerstar HQ-IR 150 W, metal halide lamp, in DMSO-*d*<sub>6</sub>. A water bath was used for cooling during the irradiation. Quantitative yields were obtained after irradiating an NMR sample of **3a** for 2 minutes. IR:  $\tilde{\nu} = 3460$  (s,br), 3057 (w), 2989 (m), 2869 (m), 1982 (w,b), 1636 (w,b), 1601 (w), 1498 (w), 1445 (w), 1392 (w), 1383 (w), 1360 (w), 1323 (w), 1293 (w), 1244 (w), 1142 (s), 1071 (w), 1021 (w), 931 (w), 902 (w), 822 (w), 782 (w), 745 (w), 696 (w), 667 (w), 575 (w), 531 (w), 471 (w), 464 (w), 449 (w), 440 (w), 429 (w), 422 (w), 414 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.20 – 7.05 (m, 6H), 6.98 (m, 4H), 2.37 (dq, J = 11.2, 1.2 Hz, 1H), 2.27 (dd, J = 4.6, 1.0 Hz, 2H), 2.07 (dq, J = 11.4, 1.3 Hz, 1H), 1.93 – 1.87 ppm (m, 2H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  138.7 (ArC), 128.5 (ArC), 128.3 (ArC), 126.0 (ArC), 34.9 (C1 and C4), 33.4 (C2 and C3), 32.3 (C7), 22.0 ppm (C5 and C6).

### 1-(4-methoxyphenyl)-5-phenyltetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]-heptane (4b)

**4b** was obtained from **3b** after irradiation by a Osram Powerstar HQ-IR 150 W, metal halide lamp, in DMSO-*d*<sub>6</sub>. A water bath was used for cooling during the irradiation. Quantitative yields were obtained after irradiating an NMR sample of **3b** for 2 minutes. IR:  $\tilde{\nu}$  = 2989 (m), 2870 (m), 1977 (w,br), 1601 (w), 1514 (w), 1449 (w), 1392 (w), 1360 (w), 1286 (w), 1244 (w), 1142 (s), 1072 (w), 1028 (w), 944 (w), 834 (w), 752 (w), 698 (w), 657 (w), 540 (w), 498 (w), 465 (w), 453 (w), 441 (w), 432 (w), 419 (w), 405 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.16 – 7.09 (m, 2H), 7.08 – 7.01 (m, 1H), 7.00 – 6.89 (m, 4H), 6.78 – 6.70 (m, 2H), 3.67 (s, 3H), 2.35 (dt, J = 11.2, 1.4 Hz, 1H), 2.26 (dd, J = 4.9, 2.5 Hz, 1H), 2.16 (dd, J = 4.9, 2.5 Hz, 1H), 2.05 (dt, J = 11.2, 1.4 Hz, 1H), 1.85 (dt, J = 4.7, 1.5 Hz, 1H), 1.81 ppm (dt, J = 4.9, 1.5 Hz, 1H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  157.9 (ArC-OMe), 139.0 (ArC), 130.2 (ArC), 130.2 (ArC), 128.2 (ArC), 128.0 (ArC), 125.7 (ArC), 113.8 (ArC), 55.4 (CH<sub>3</sub>), 34.9(C1), 34.3 (C4), 34.0 (C2), 32.4 (C3), 32.2 (C7), 22.0 (C5), 21.2 (C6) ppm.

### 1-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane (4c)

**4c** was obtained from **3c** after irradiation by a Osram Powerstar HQ-IR 150 W, metal halide lamp, in DMSO-*d*<sub>6</sub>. A water bath was used for cooling during the irradiation. Quantitative yields were obtained after irradiating an NMR sample of **3c** for 2 minutes. IR:  $\tilde{\nu}$  = 2989 (m), 2870 (m), 2294 (w,br), 1976 (w,b), 1613 (w), 1516 (w), 1449 (w), 1392 (m), 1360 (w), 1325 (w), 1295 (w), 1246 (w), 1142 (s), 1071 (w), 930 (w), 834 (w), 668 (w), 593 (w), 516 (w), 452 (w), 438 (w), 418 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.49 – 7.43 (m, 2H), 7.06 – 7.01 (m, 4H), 6.81 – 6.75 (m, 2H), 3.69 (s, 3H), 2.43 (dd, J = 5.0, 2.5 Hz, 1H), 2.38 (dt, J = 11.3, 1.4 Hz, 1H), 2.20 (dd, J = 4.9, 2.5 Hz, 1H), 2.08 (dt, J = 11.3, 1.4 Hz, 1H), 2.00 (dq, J = 5.0, 1.4 Hz, 1H), 1.87 ppm (dt, J = 4.9, 1.5 Hz, 1H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  158.1 (ArC-OMe), 130.6 (ArC), 129.6 (ArC), 127.9 (ArC), 125.1 (ArC), 125.0 (ArC-CF<sub>3</sub>), 114.0 (ArC), 55.4 (CH<sub>3</sub>), 35.7 (C1), 34.3 (C4), 32.3 (C2), 31.9 (C3), 23.8 (C5), 21.1 ppm (C6). <sup>19</sup>F-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  -60.63 ppm.



#### 4-(5-(4-methoxyphenyl)tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptan-1-yl)benzotrile (4d)

**4d** was obtained from **3d** after irradiation by a Osram Powerstar HQ-IR 150 W, metal halide lamp, in DMSO-*d*<sub>6</sub>. A water bath was used for cooling during the irradiation. Quantitative yields were obtained after irradiating an NMR sample of **3d** for 2 minutes. IR:  $\tilde{\nu}$  = 3462 (s,br), 2988 (m), 2869 (m), 2224 (w), 1605 (m), 1515 (m), 1384 (m), 1260 (m), 1245 (m), 1142 (s), 1024 (m), 799 (m), 668 (w), 557 (w), 497 (w), 453 (w), 439 (w), 425 (w), 409 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.58 – 7.52 (m, 2H), 7.08 – 7.03 (m, 2H), 6.99 – 6.94 (m, 2H), 6.82 – 6.78 (m, 2H), 3.69 (s, 3H), 2.48 – 2.46 (m, 1H), 2.38 (dt, J = 11.3, 1.4 Hz, 1H), 2.20 (dd, J = 4.9, 2.5 Hz, 1H), 2.11 – 2.05 (m, 2H), 1.86 ppm (dq, J = 5.1, 1.5 Hz, 1H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  158.2 (ArC-OMe), 146.2 (ArC), 132.0 (ArCH), 130.8 (ArC), 129.4 (ArCH), 127.7 (ArCH), 119.6 (CN), 114.1 (ArCH), 107.6 (ArC-CN), 55.4 (CH<sub>3</sub>), 36.6 (C1), 35.2 (C4), 34.2 (C2), 32.3 (C3), 31.8 (C7), 25.1 ppm (C6), 21.1 (C5).

#### N,N-dimethyl-4-(5-(4-(trifluoromethyl)phenyl)tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptan-1-yl)aniline (4e)

**4e** was obtained from **3e** after irradiation by a Osram Powerstar HQ-IR 150 W, metal halide lamp, in DMSO-*d*<sub>6</sub>. A water bath was used for cooling during the irradiation. Quantitative yields were not reached, a consequence of the fast back reaction even at room temperature. Rather 40-75% yields were observed depending on the time between isomerisation and NMR measurement. IR:  $\tilde{\nu}$  = 3459 (s,br), 2989 (m), 2869 (m), 1978 (w), 1638 (m,b), 1522 (w), 1449 (w), 1392 (w), 1360 (w), 1324 (w), 1142 (s), 1067 (w), 944 (w), 715 (w), 452 (w), 429 (w), 414 (w) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.49 – 7.42 (m, 2H), 7.08 – 7.02 (m, 2H), 6.99 – 6.91 (m, 2H), 6.63 – 6.54 (m, 2H), 2.82 (s, 6H), 2.41 (dd, J = 4.9, 2.5 Hz, 1H), 2.36 (dt, J = 11.2, 1.4 Hz, 1H), 2.12 (dd, J = 4.9, 2.5 Hz, 1H), 2.07 (dt, J = 11.3, 1.4 Hz, 1H), 1.97 (dt, J = 5.1, 1.5 Hz, 1H), 1.80 ppm (dt, J = 4.9, 1.5 Hz, 1H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  149.4 (ArC-N), 145.0 (ArC), 130.4 (ArCH), 127.6 (ArC-CF<sub>3</sub>), 125.9 (ArCH), 125.0 (ArC), 124.9 (ArCH), 124.8 (CF<sub>3</sub>), 112.5 (ArCH), 40.6 (N(CH<sub>3</sub>)<sub>2</sub>), 36.1 (C1), 34.9 (C4), 34.4 (C2), 32.3 (C3), 24.0 (C6), 20.9 ppm (C5). <sup>19</sup>F-NMR (DMSO-*d*<sub>6</sub>, 400 MHz):  $\delta$  -60.61 ppm.

## Photo-isomerization

Photo-isomerization was also followed by UV/Vis absorption spectroscopy, figure S2. Spectra were recorded on a Cary 4000 or Cary 50 Bio UV/Vis spectrophotometer in a 1 mm quartz cuvette. Figure S2a) shows the absorption decrease following the isomerization of norbornadiene **3a** to quadricyclane **4a**, in acetonitrile, when irradiated by an Osram Powerstar HQI-R 150 W, metal halide lamp. Similarly spectra in S2b) and c) follows the isomerization of **3b** and **3c** in acetonitrile while irradiating at 308 nm and 316 nm respectively (FWHM = 21.3 nm). Norbornadienes **3d** and **3e** were isomerized in toluene at 366 nm (FWHM = 10.7 nm), figures S2d) and e).

## Isomerization Quantum Yield

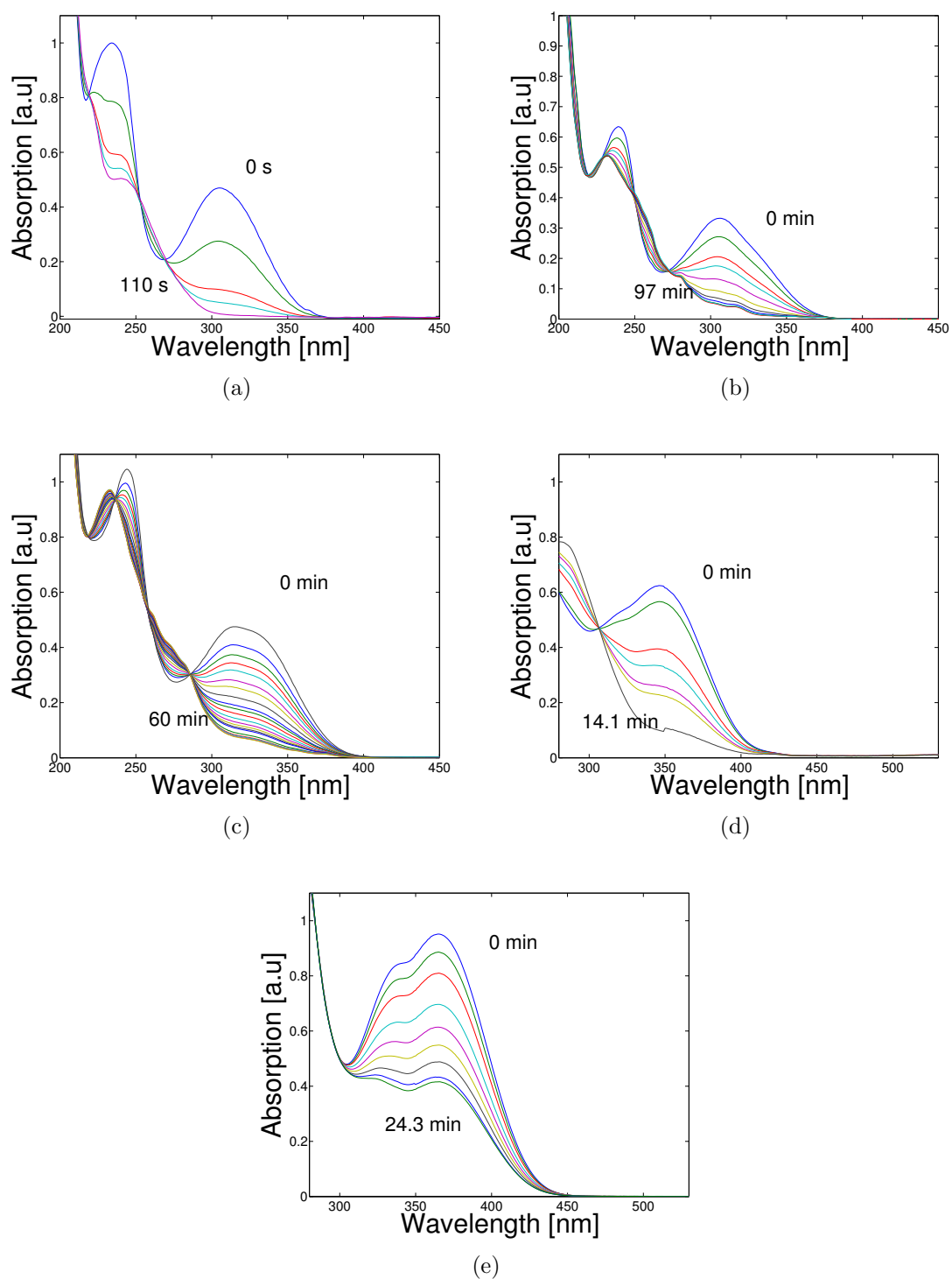
Isomerization quantum yields were determined at 366 nm (FWHM=10.7nm) in toluene (**3a-e**) using a 10 mm path-length quartz cuvettes and a Spex Fluorolog  $\tau$ 2 spectrofluorometer. Potassium ferrioxalate actinometry was used to determine the quantum flow<sup>3,4</sup> to 2.16 nE/s. The extent of isomerisation was followed by absorption and <sup>1</sup>H-NMR spectroscopy respectively.

## Cyclability test

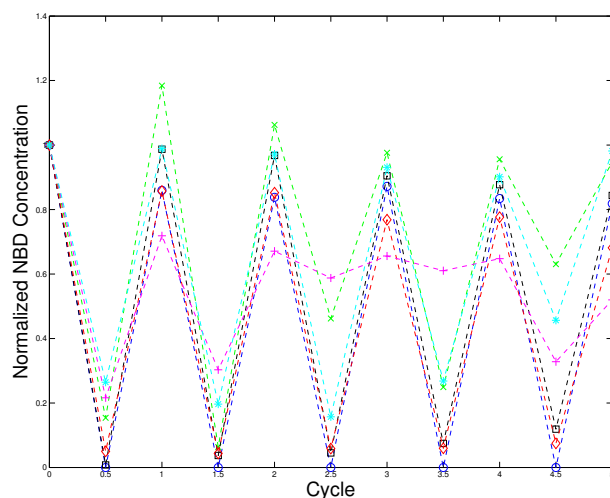
A few milligrams of norbornadienes **3a-e** were dissolved in DMSO-*d*<sub>6</sub> in an NMR-tube. The samples were placed in a cooling-bath with water and irradiated for 2-30 minutes by an Osram Powerstar HQI-R 150 W, metal halide lamp. The thermal reversed isomerization was activated by heating the samples to 70-90°C for 3-12 h. Conversions were measured by <sup>1</sup>H-NMR integration using the residual proton resonance in DMSO-*d*<sub>6</sub> as standard. This sequence was performed 5 times and the results depicted in figure S3. A degassed sample of norbornadiene **3e** was prepared by four freeze-pump-thaw cycles prior to the cycling experiment.

## Eyring and Arrhenius plots

The samples for determining the thermal reverse reaction were prepared directly in a cuvette. An absorption of 0.18-0.36, at the absorption maximum, was sought for each compound. The solvent used was toluene and a Teflon cap was needed to prevent evaporation of solvent during the experiment. After preparation, the samples were degassed with nitrogen for 15 minutes and photoconverted by exposure to an Osram Powerstar HQI-R 150 W, metal



**Figure S2:** Normalized absorption for varying irradiation times. a) **3a** irradiated by a metal halide lamp in acetonitrile, b) **3b** irradiated at 308 nm in acetonitrile, c) **3c** irradiated at 316 nm in acetonitrile, d) **3d** irradiated at 366 nm in toluene and e) **3e** irradiated at 366 nm in toluene



**Figure S3:** Cyclability of **3a-e**; **3a**(o), **3b**(x), **3c**(□) **3d**(◇), **3e**(+) and **3e** (degassed, \*)

halide lamp for 2 minutes. In this case the cuvette was also placed in a water bath for cooling.

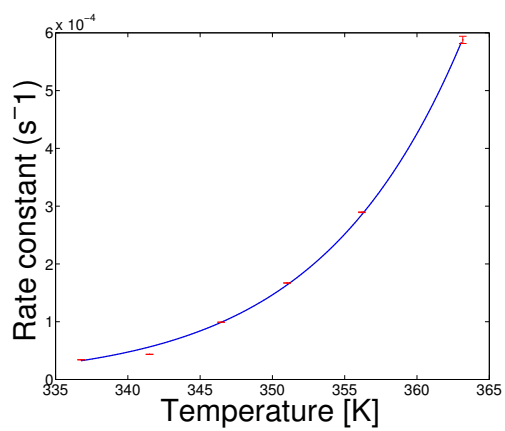
The reaction rate could be observed by measuring the absorbance increase at 312 nm, 313 nm, 324 nm, 347 nm and 366 nm for molecules **3a**, **3b**, **3c**, **3d** and **3e** respectively. Absorbance measurements were performed using a Cary 4000 spectrophotometer equipped with a temperature regulated sample changer. Temperature was continuously measured in a reference cuvette filled with water.

The concentration decrease of the metastable isomer was fitted to first order kinetics, according to equation 1, where  $C$  is the concentration at the starting point,  $k$  is the rate constant ( $s^{-1}$ ) and  $t$  is the time (s). As the concentration is directly proportional to the absorbance the fitting could be done directly to the absorbance data. Before the fitting was done the absorbance was normalized.

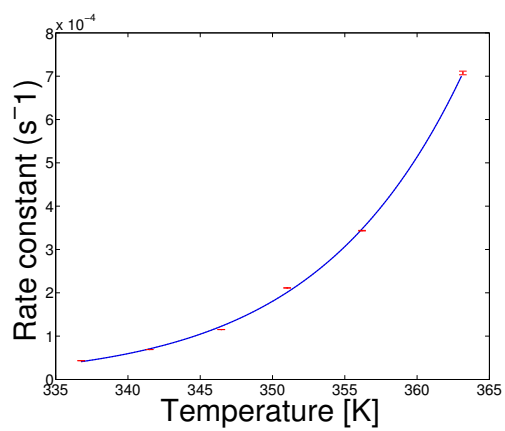
$$y = Ce^{-kt} \quad (1)$$

Fitting was done using an in-house made Matlab script. The obtained rate constants were then used to calculate the activation energy and enthalpy of activation by fitting them to the Arrhenius and Eyring equation respectively. Curves fitted to the measured rate constants are seen in figures S4. Data of norbornadienes **3c** and **3e** were more widely spread, especially at higher temperatures, compared to the other norbornadienes. This is most

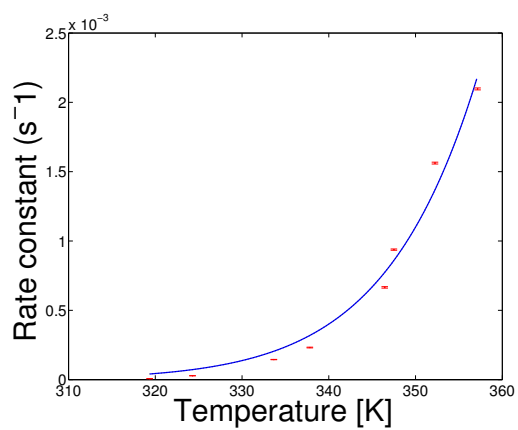
probably a consequence of the shorter lifetimes of the photoisomers and thus the considerably much faster kinetics at higher temperatures. Therefore the time it takes to equilibrate with the surrounding heating block is a large part of the measurement time.



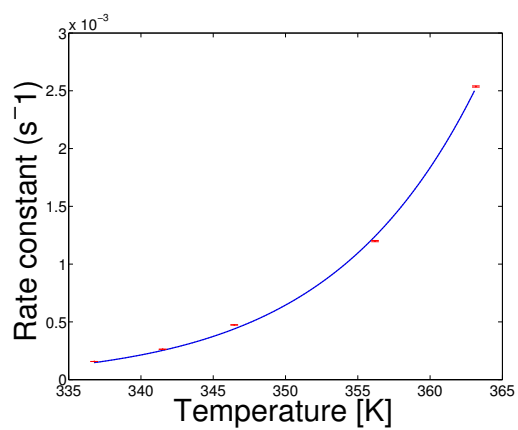
(a)



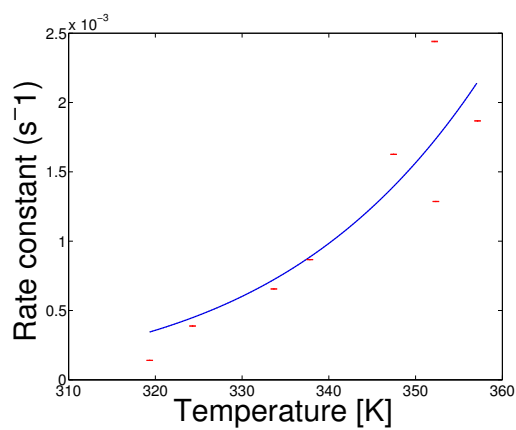
(b)



(c)



(d)

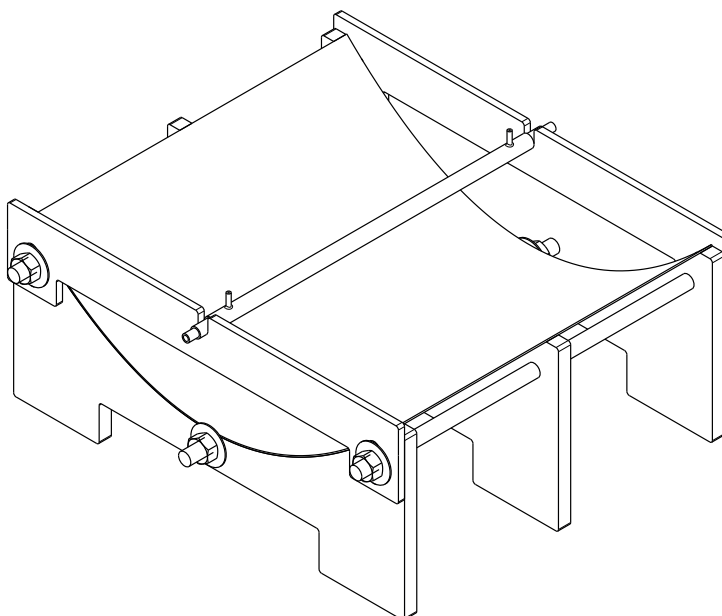


(e)

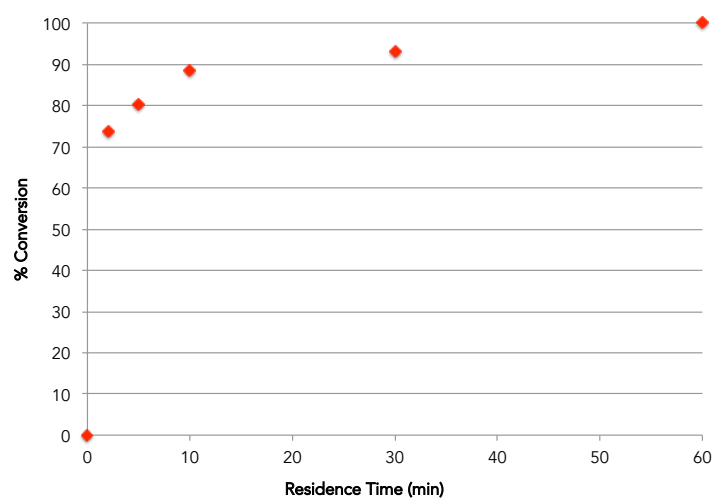
**Figure S4:** Fitted Arrhenius (---) and Eyring (—) equations to measured rate constants (red dots) for a) **3a**, b) **3b**, c) **3c**, d) **3d** and e) **3e**.

## Demonstration with a Solar-Collector

A parabolic trough solar-collector was manufactured at the department of Mechanical Engineering at Chalmers University of Technology. The reflector was produced from a commercially available 1-mm thick aluminum sheet laminated with 3M solar mirror film from TA Industrial Solutions, Inc. A detailed isometric drawing of the device is shown in figure S5. A 25 ml toluene solution with 0.1 % (w/v) of norbornadiene **3c** was continuously pumped through the glass pipe. A solar-simulator (EYE Lighting International 93510) was used as the light source. Experiments were run with different residence times and the conversion was followed by UV/VIS spectroscopy at 350 nm. The amount of conversion as a function of residence time is displayed in figure S6.



**Figure S5:** Isometric drawing of the solar-collector.



**Figure S6:** Percentage of norbornadiene to quadricyclane conversion with varying residence times.



## References

- [1] G. K. Tranmer, C. Yip, S. Handerson, R. W. Jordan and W. Tam, *Can. J. Chem.*, 2000, **78**, 527–535.
- [2] W.-J. Yoo, G. C. Tsui and W. Tam, *New J. Chem.*, 2005, **2005**, 1044–1051.
- [3] C. A. Parker, *Proc. R. Soc. A*, 1953, **220**, 104–116.
- [4] C. G. Hatchard and C. A. Parker, *Proc. R. Soc. A*, 1956, **235**, 518–536.