SUPPORTING INFORMATION

IMMOBILIZATION OF A PHOTOSWITCHABLE PIPERIDINE BASE

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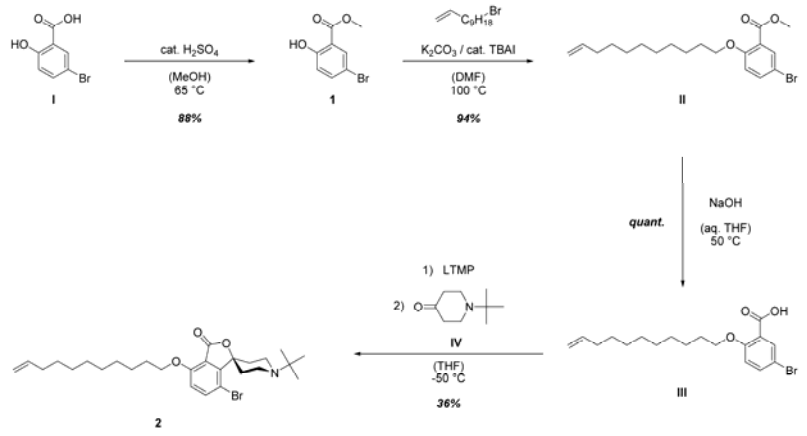
General Methods

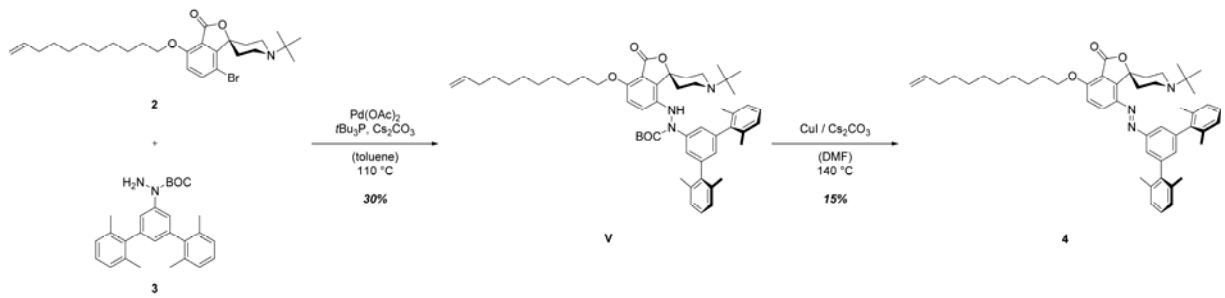
Solvents and starting materials were used as received. Toluene and THF were distilled under an argon atmosphere over sodium prior to use. Dry DMF was purchased from Acros. All reactions were performed in an argon atmosphere. Column chromatography was carried out with 130 - 400 mesh silica gel. NMR spectra were recorded on a 400 MHz (100.6 MHz for ^{13}C) Bruker AV 400 or on a 300 MHz (75.6 MHz for ^{13}C) Bruker DPX 300 spectrometer at 27 °C using residual protonated solvent signals as internal standard (^{1}H-NMR: $\delta(CDCl_3) = 7.24$ ppm, $\delta(CD_2Cl_2) = 5.30$ ppm and ^{13}C-NMR: $\delta(CDCl_3) = 77.0$ ppm, $\delta(CD_2Cl_2) = 53.52$ ppm). Mass spectrometry was performed on Thermo LTQ FT instrument (ESI, ESI-HRMS: additives of mixtures of MeOH/H_2O 75/25 + 0.5% formic acid) and MSI concept 1H (EI, 70eV ionization) as well as on a QSTARXL Applied Q-TOF with a ISV of 950 V. HPLC separations were performed with Shimadzu LC-10A systems equipped with a photodiode array detector (PAD or DAD) or with Waters Alliance systems (mixtures and gradient mixtures of acetonitrile/water) equipped with 150 x 2 mm Luna columns (3 µm, phenyl-hexyl material). The Waters systems consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996 and a Waters Mass Detector ZQ 2000. Conditions are specified when describing the corresponding substances. UPLC separations were preformed with a Waters Acquity system equipped with Acquity UPLC columns, a Waters Diode Array detector, and a LCT PremierXE TOF-MS detector.

Synthesis

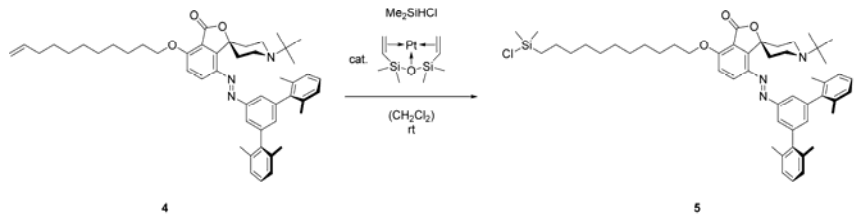
Synthesis of Spiro Precursor **2**



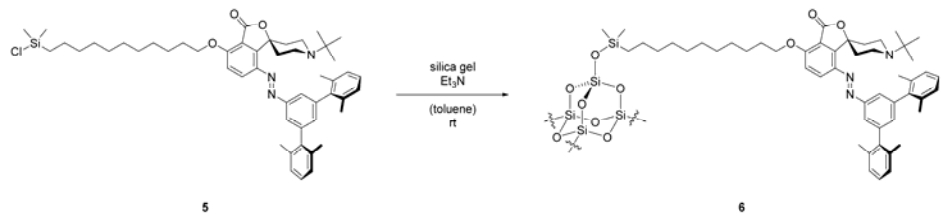
Synthesis of Immobilization Precursor **4**



Hydrosilylation



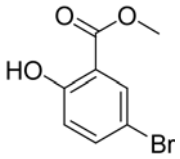
Immobilization on Silica Gel



Scheme 1. Synthesis of azo-spirocompound *E*-**6**.

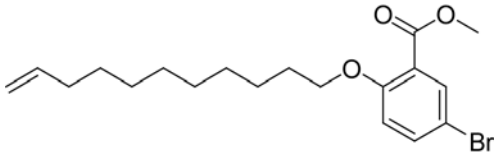
Experimental Procedures

Methyl 5-bromo-2-hydroxybenzoate **1**



5-Bromo-2-hydroxybenzoic acid **I** (21.70 g, 100.0 mmol) was dissolved in 50 mL of methanol and 10 mL of conc. sulfuric acid were added in portions. The mixture was heated to reflux for 6 h. The mixture was poured on ice and the aqueous layer was extracted with methylene chloride three times. Combined organic layers were washed with sat. aq. $NaHCO_3$-solution and brine three times, respectively, and subsequently dried over $MgSO_4$. Removal of solvent afforded 20.28 g of product as a colorless solid (88.0 mmol, 88%). R_f (CH_2Cl_2/Hex, 2/8) = 0.28. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 10.69 (s, 1H, O*H*), 7.94 (d, ^{4}J = 2.5 Hz, 1H, Ar-*H*), 7.51 (dd, ^{3}J = 8.9 Hz, ^{4}J = 2.53 Hz, 1H, Ar-*H*), 6.88 (d, ^{3}J = 8.9 Hz, 1H, Ar-*H*), 3.95 (s, 3H, C*H*$_3$). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 169.6, 169.7, 138.5, 132.3, 119.7, 113.9, 110.9, 52.7. DEPT135-NMR ($CDCl_3$): δ (ppm) =138.5 (pos.), 132.2 (pos.), 119.7 (pos.), 52.73 (pos.). MS (ESI neg.): *m/z* = 231 ([M - H]$^-$), 229 ([M - H]$^-$). HRMS (ESI neg.): *m/z* = 228.9503 (calc. 228.9506 for $C_8H_6O_3{}^{79}Br$). UPLC (gradient 5→50% CH_3CN/H_2O): t_R = 6.95 min (90% peak area).

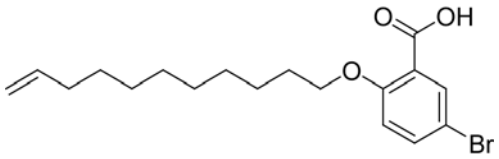
Methyl 5-bromo-2-(undec-10-enyloxy)benzoate **II**



Methyl 5-bromo-2-hydroxybenzoate **1** (11.55 g, 50.0 mmol), K_2CO_3 (16.59 g, 120.0 mmol), and tetrabutylammonium iodide (1.85 g, 0.1 mmol) were dissolved in 80 mL of dry DMF and 11-bromo-1-undecane was added to the stirring mixture. The mixture was heated to 100 °C for 18 h and the majority of the solvent was subsequently removed by vacuum distillation. The residue was dissolved in water and the aqueous layer was extracted with methylene chloride three times. Combined organic layers were washed with brine three times, dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification of the residue by column chromatography (silica gel, CH_2Cl_2/Hex, 3/7) afforded the product as a colorless solid (18.07 g, 94%).). R_f (CH_2Cl_2/Hex, 3/7) = 0.20. ^{1}H-NMR ($CDCl_3$,

300 MHz): δ (ppm) = 7.87 (d, ^{4}J = 2.43 Hz, 1H, Ar-*H*), 7.48 (dd, ^{3}J = 8.85 Hz, ^{4}J = 2.43 Hz, 1H, Ar-*H*), 6.81 (d, ^{3}J = 8.85 Hz, 1H, Ar-*H*), 5.86-5.72 (m, 1H, =C*H*), 5.00-4.89 (m, 2H, =C*H*), 3.97 (t, ^{3}J = 6.5 Hz, 2H, C*H*$_2$), 3.86 (s,3H, C*H*$_3$), 2.05-1.99 (m, 2H, C*H*$_2$), 1.84-1.75 (m, 2H, C*H*$_2$), 1.45-1.29 (m, 10H, C*H*$_2$). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 165.54, 157.82, 139.20, 135.96, 134.19, 122.07, 115.01, 114.21, 112.02, 69.30, 52.17, 33.86, 29.56, 29.47, 29.35, 29.17, 29.11, 28.98, 25.93. DEPT135-NMR ($CDCl_3$): δ (ppm) = 139.20 (pos.), 135.96 (pos.), 134.19 (pos.), 115.01 (pos.), 114.21 (neg.), 69.30 (neg), 52.17 (neg.), 33.86 (neg.), 29.56 (neg.), 29.47 (neg.), 29.34 (neg.), 29.17 (neg.), 29.10 (neg.), 28.98 (neg.), 25.86 (neg.). MS (ESI pos.): *m/z* = 385 ([M + H]$^+$), 383 ([M + H]$^+$). HRMS (ESI pos.): *m/z* = 383.1221 (calc. 383.1219 for $C_{19}H_{28}O_3{}^{79}Br$). UPLC (gradient 40→95% CH_3CN/H_2O): t_R = 5.33 min (95% peak area).

5-Bromo-2-(undec-10-enyloxy)benzoic acid **III**



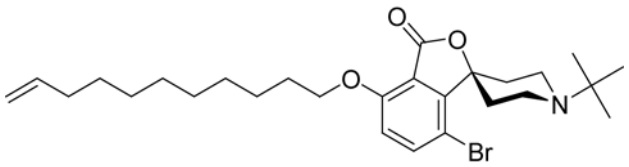
Methyl 5-bromo-2-(undec-10-enyloxy)benzoate **II** (3.71 g, 9.68 mmol) was dissolved in a mixture of 50 mL of THF and 25 mL of water. Addition of sodium hydroxide (6.78 g, 169.37 mmol) was followed by stirring at 50 °C for 16 h. The mixture was adjusted to acidic pH using conc. aq.-HCl. Phases were separated and the aqueous layer was extracted with ethyl acetate three times. Combined organic layers were washed with brine three times, dried over $MgSO_4$, and the solvent was removed *in vacuo*. Recrystallization of the crude material from cold hexane afforded pure product as a colorless solid (3.57 g, 100%). R_f (Hex/EA, 8/2) = 0.16. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 10.54 (s, broad, 1H, CO_2*H*), 8.24 (d, ^{4}J = 2.63 Hz, 1H, Ar-*H*), 7.61 (dd, ^{3}J = 8.86 Hz, ^{4}J = 2.63 Hz, 1H, Ar-*H*), 6.93 (d, ^{3}J = 8.86 Hz, 1H, Ar-*H*), 5.85-5.72 (m, 1H, =C*H*), 5.01-4.88 (m, 2H, =C*H*), 4.21 (t, ^{3}J = 6.6 Hz, 2H, C*H*$_2$), 2.05-2.01 (m, 2H, C*H*$_2$), 1.98-1.84 (m, 2H, C*H*$_2$), 1.51-1.23 (m, 12H, C*H*$_2$). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 164.42, 156.74, 139.19, 137.64, 136.12, 119.41, 114.61, 114.48, 114.25, 70.79, 33.84, 29.41, 29.39, 29.22, 29.11, 28.94, 28.89, 25.86. DEPT135-NMR ($CDCl_3$): δ (ppm) = 139.19 (pos.), 137.64 (pos.), 136.12 (pos.), 114.61 (pos.), 114.25 (neg.), 70.79 (neg.), 33.84 (neg.), 29.41 (neg.), 29.39 (neg.), 29.22 (neg.), 29.11 (neg.), 28.94 (neg.), 28.89 (neg.), 25.86 (neg.). MS (ESI pos.): *m/z* = 371 ([M + H]$^+$), 369 ([M + H]$^+$). HRMS (ESI pos.): *m/z* = 369.1055 (calc. 369.1060 for $C_{18}H_{26}O_3{}^{79}Br$). UPLC (gradient 50→95% CH_3CN/H_2O): t_R = 5.72 min (98% peak area).

N-tert-Butylpiperidone **IV**

N-tert-Butylpiperidone **IV** was synthesized according to the literature.[1]

Spiroannulated Piperidine **2**

Syntheses of spiroannulated piperidine **2** as inspired by the procedures developed by Gohier et al.[2] and Parham et al.[3]



A dry Schlenk tube was charged with tetramethylpiperidine (4.63 mL, 27.21 mmol) and 16 mL of dry THF. The mixture was cooled to 0 °C, *n*-butyl lithium (1.6 M in hexanes, 17.01 mL, 27.21 mmol) were added dropwise, and the mixture was stirred at 0 °C for 1 h. After cooling to -50 °C, a solution of 5-bromo-2-(undec-10-enyloxy)benzoic acid **III** (4.57 g, 12.37 mmol) in 15 mL of dry THF was added dropwise over the course of 10 min. Stirring at -50 °C was continued for 7 min and a solution of *tert*-butyl piperidone **IV** (3.84 g, 24.74 mmol) in 5 mL of dry THF was added dropwise. After stirring at -50 °C for 1 h, the mixture was allowed to warm to room temperature and stirring was continued for 1 h. The mixture was quenched with 1N aq. HCl-solution, acidified with conc. aq.-HCl, and stirred for 18 h at room temperature. After adjusting the mixture to basic pH by addition of sat. aq. $NaHCO_3$-solution, phases were separated and the aqueous layer was extracted with ethyl acetate three times. Combined organic layers were washed with sat. aq. $NaHCO_3$-solution and brine three times, respectively, dried over $MgSO_4$, and the solvent was removed *in vacuo* to obtain 12.37 g of a crude mixture of products. Free carboxylic acids present in the crude mixture prevented successful purification and were therefore transformed into their respective methyl ester by the following procedure. The crude product mixture was dissolved in 50 mL of methanol, cooled to 0 °C, and EDC-HCl (3.32 g, 17.32 mmol) was added together with DMAP (0.53 g, 4.33 mmol). The mixture was allowed to warm to room temperature for 18 h and the solvent was removed *in vacuo*. The residue was

[1] Stoll, R. S.; Peters, M. V.; Kühn, A.; Heiles, S.; Goddard, R.; Bühl, M.; Thiele, C. M.; Hecht, S. *J. Am. Chem. Soc.* **2009**, *131*, 357-367; Peters, M. V.; Stoll, R. S.; Kühn, A.; Hecht, S. *Angew. Chem., Int. Ed. Engl.* **2008**, *47*, 5968-5972.

[2] Gohier, F.; Mortier, J. *J. Org. Chem.* **2003**, *68*, 2030-2033.

[3] Parham, W. E.; Egberg, D. C.; Sayed, Y. A.; Thraikill, R. W.; Keyser, G. E.; Neu, M.; Montgomery, W. C.; Jones, L. D. *J. Org. Chem.* **1976**, *41*, 2628-2633.

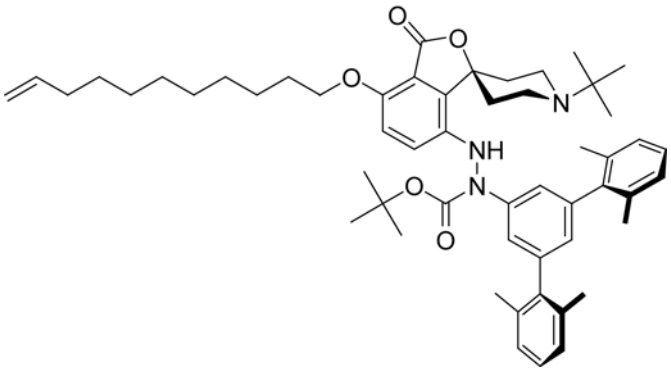
collected in methylene chloride and the organic layer was washed with 1N aq. citric acid solution three times, sat. aq. $NaHCO_3$-solution four times, and brine three times. Drying of the organic layer over $MgSO_4$ and subsequent removal of the solvent *in vacuo* afforded a crude mixture, which was purified by column chromatography (silica gel, Hex/EA, 6/4 + 0.1 vol% Et_3N) to afford the product as a colorless solid (1.72 g, 36%). R_f (Hex/EA, 6/4 + 0.1 vol% Et_3N) = 0.30. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.63 (d, ^{3}J = 8.7 Hz, 1H, Ar-*H*), 6.80 (d, ^{3}J = 8.7 Hz, 1H, Ar-*H*), 5.85-5.72 (m, 1, =C*H*), 4.99-4.89 (m, 2H, =C*H*), 4.10 (t, ^{3}J = 6.8 Hz, 2H, CH_2), 3.01-3.01 (m, 2H, CH_2), 2.83-2.75 (m, 2H, CH_2), 2.64-2.56 (m, 2H, CH_2), 2.05-2.00 (m, 2H, CH_2), 1.91-1.81 (m, 2H, CH_2), 1.55-1.28 (m, 14H, CH_2), 1.09 (s, 9H, CH_3). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 166.15, 157.88, 152.93, 140.13, 139.28, 115.98, 114.22, 113.96, 105.43, 85.19, 69.44, 54.14, 42.19, 33.88, 33.59, 29.51, 29.47, 29.36, 29.18, 28.98, 28.80, 26.35, 25.83. DEPT135-NMR ($CDCl_3$): δ (ppm) = 140.13 (pos.), 139.28 (pos.), 114.22 (neg.), 113.96 (pos.), 69.44 (neg.), 42.19 (neg.), 33.88 (neg.), 33.59 (neg.), 29.51 (neg.), 29.47 (neg.), 29.36 (neg.), 29.18 (neg.), 28.98 (neg.), 28.80 (neg.), 26.35 (neg.), 25.83 (neg.). MS (ESI pos.): *m/z* = 508 ($[M + H]^+$), 506 ($[M + H]^+$). HRMS (ESI pos.): *m/z* = 506.2267 (calc. 506.2264 for $C_{27}H_{41}O_3N^{79}Br$). UPLC (gradient 50→95% CH_3CN/H_2O): t_R = 3.30 min (96% peak area).

BOC-Hydrazo Building Block **3**

BOC-Hydrazo building block **3** was prepared according to the literature.[1]

Diarylhydrazine **V**

Diarylhydrazine **V** was synthesized following a protocol developed by Lim et al.[4]

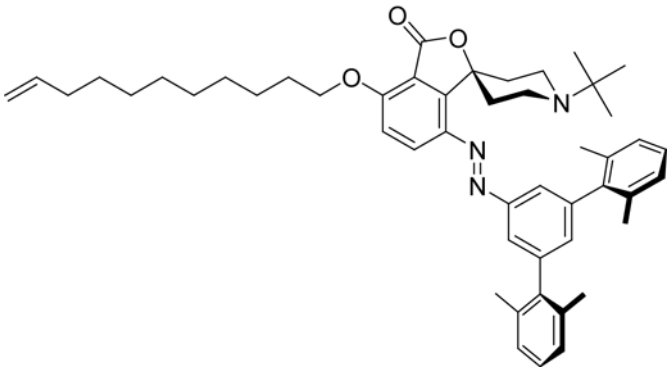


A dry sealable tube was charged with spiroannulated piperidine **2** (483 mg, 0.952 mmol), 1-*tert*-butoxycarbonyl-1-(3,5-bis(2,6-dimethylphenyl)phenyl)hydrazine **3** (476 mg, 1.144 mmol), palladium(II) acetate (43 mg, 0.191 mmol), tri-*tert*-butylphosphine (solution in toluene, 39 mg, 0.191 mmol), ceasium carbonate (621 mg, 1.906 mmol), and 10 mL of dry toluene. The tube was sealed and heated to 120 °C for 21 h. The mixture was passed through a plug of Celite using methylene chloride and the solvent was removed *in vacuo*. Purification of the raw material by column chromatography (silica gel, gradient CH_2Cl_2/MeOH, 9.9/0.1→9.8/0.2 + 0.1 vol% Et_3N) afforded the product as a colorless solid (240 mg, 30%). R_f (CH_2Cl_2/MeOH, 9.8/0.2 + 0.1 vol% Et_3N) = 0.30. ^{1}H-NMR: despite repeated attempts no conclusive ^{1}H-NMR of the title compound could be obtained. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 167.26, 153.83, 152.53, 142.85, 141.55, 141.43, 136.04, 135.56, 131.04, 135.56, 131.75, 130.96, 127.41, 127.24, 126.51, 124.65, 123.72, 121.32, 118.84, 113.80, 82.69, 69.48, 46.33, 42.40, 32.69, 29.70, 29.51, 29.44, 29.32, 29.21, 29.06, 28.34, 26.93, 26.21, 25.93, 21.01, 18.04. DEPT135-NMR ($CDCl_3$): δ (ppm) = 131.75 (pos.), 130.96 (pos.), 127.41(pos.), 127.24 (pos.), 126.51 (pos.), 124.65 (pos.), 121.32 (pos.), 118.87 (pos.), 113.80 (pos.), 69.48 (neg.), 46.33 (neg.), 42.40 (neg.), 32.69 (neg.), 29.70 (neg.), 29.51 (neg.), 29.44 (neg.), 29.32 (neg.), 29.21 (neg.), 29.06 (neg.), 28.34 (pos.), 26.93 (neg.), 26.21 (pos.), 25.93 (neg.), 21.01 (pos.), 18.04 (pos.). MS (ESI pos.): *m/z* = 842 ($[M + H]^+$). HRMS (ESI pos.): *m/z* = 842.5458 (calc. 842.5466 for $C_{54}H_{72}O_5N_3$). UPLC (gradient 50→90% CH_3CN/H_2O): t_R = 5.08 min (91% peak area).

[4] Lim, Y.-K.; Lee, K.-S.; Cho, C.-G. *Org. Lett.* **2003**, *5*, 979-982.

Immobilization Precursor **4**

Immobilization precursor **4** was synthesized adopting a procedure by Lim et al.[5]

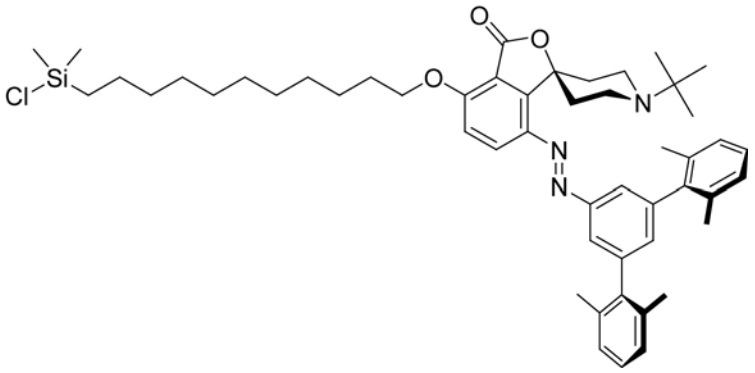


A dry sealable tube was charged with diarylhydrazine **V** (75 mg, 0.089 mmol), copper(I) iodide (25 mg, 0.134 mmol), ceasium carbonate (43 mg, 0.134 mmol), and 1 mL of dry DMF. The tube was flushed with argon several times, sealed, and heated to 140 °C for 8 h. The mixture was passed through a plug of Celite using methylene chloride and the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 9.9/0.1 + 0.1 vol% Et_3N) to afford the product as an orange solid (10 mg, 15%). An additional fraction of slightly impure product could be isolated as well (14 mg). The samples obtained could be further purified by repeated recrystallization from methanol. R_f (CH_2Cl_2/MeOH, 9.7/0.3 + 0.1 vol% Et_3N) = 0.34. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 8.04 (d, ^{3}J = 9.0 Hz, 1H, Ar-*H*), 7.72 (d, ^{4}J = 1.6 Hz, 2H, Ar-*H*), 7.18-7.09 (m, 6H, Ar-*H*), 7.08 (t, ^{4}J = 1.6 Hz, 1H, Ar-*H*), 7.00 (d, ^{3}J = 9.0 Hz, 1H, Ar-*H*), 5.42-5.38 (m, 3H, =C*H*), 4.19 (t, ^{3}J = 6.7 Hz, 2H, CH_2), 2.98-2.94 (m, 2H, CH_2), 2.72-2.62 (m, 2H, CH_2), 2.52-2.44 (m, 2H, CH_2), 2.14 (s, 12H, CH_3), 2.09-1.84 (m, 6H, CH_2), 1.77-1.72 (m, 2H, CH_2), 1.54-1.26 (m, 10H, CH_2), 0.90 (s, 9H, CH_3). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 166.56, 160.48, 154.91, 153.41, 142.54, 141.01, 139.40, 135.88, 133.01, 131.72, 130.89, 127.51, 127.36, 124.56, 122.43, 114.24, 112.64, 85.00, 69.64, 42.83, 37.87, 32.66, 29.70, 29.63, 29.48, 29.35, 29.19, 28.95, 26.87, 25.98, 25.84, 20.88. DEPT135-NMR ($CDCl_3$): δ (ppm) = 133.01 (pos.), 131.72 (pos.), 127.51 (pos.), 127.36 (pos.), 124.56 (pos.), 122.43 (pos.), 112.64 (pos.), 69.64 (neg.), 42.83 (neg.), 37.87 (neg.), 32.66 (neg.), 29.70 (neg.), 29.63 (neg.), 29.48 (neg.), 29.35 (neg.), 29.19 (neg.), 28.95 (neg.), 26.87 (neg.), 25.98 (pos.), 25.84 (neg.), 20.88 (pos.). MS (ESI pos.): *m/z* = 741 ($[M + H]^+$). HRMS (ESI pos.): *m/z* = 740.4789 (calc. 740.4791 for $C_{49}H_{62}O_3N_3$). UPLC (gradient 60→95% CH_3CN/H_2O): t_R = 4.47 min (100% peak area).

[5] Lim, Y.-K.; Choi, S.; Park, K. B.; Cho, C.-G. *J. Org. Chem.* **2004**, *69*, 2603-2606.

Monochlorosilane **5**

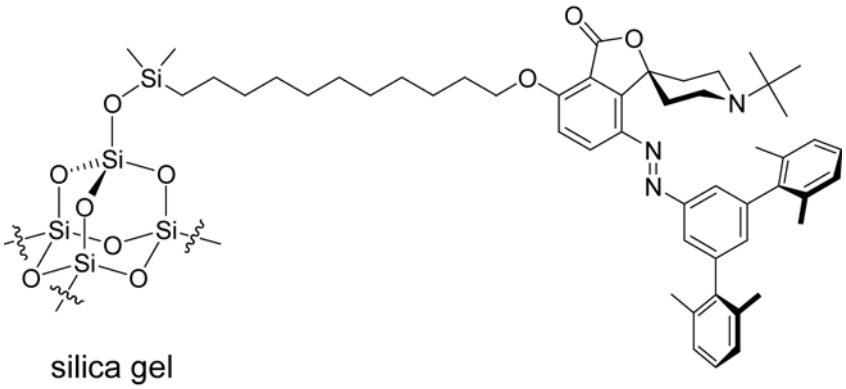
Monochlorosilane **5** was synthesized adopting a synthesis described by Tully et al.[6]



A dry Schlenk tube was charged with 10 mg of immobilization precursor **4** (0.013 mmol, 1 equiv.), one drop of Karsted's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 0.10 M solution in xylene), and 1 mL of methylene chloride under an atmosphere of argon. The mixture was stirred at room temperature for 25 min and 145 µL dimethylchlorosilane (1.30 mmol, 100 equiv.) were added in one portion. The mixture was stirred for 18 h at room temperature. The solvent was removed *in vacuo* and the orange material obtained was directly used without further characterization.

Supported Catalyst **6**

Supported catalysts were synthesized adopting a procedure described by Tully et al.[6]



A dry Schlenk flask was charged with 11 mg of monochlorsilane **23** (0.013 mmol), 200 mg of silica gel (as received), and 2 mL of dry toluene. After addition of 3 drops of dry triethyl amine, the mixture was stirred under an atmosphere of argon at room temperature for 24 h. The solid was collected by centrifugation and extensively washed with toluene, ethyl acetate, and methylene chloride/methanol

[6] Tully, D. C.; Wilder, K.; Fréchet, J. M. J.; Trimble, A. R.; Quate, C. F. *Adv. Mater.* **1999**, *11*, 314-318.

mixtures, respectively. The gray powder was dried *in vacuo*. For characterization by UV/vis spectroscopy, see MS Figure 3.

The approximate loading of **6** on silica gel was estimated using the UV/vis spectra in methylene chloride (see MS Figure 3). Assuming a quantitative photochemical $E \rightarrow Z$ isomerization of *E*-**6** and negligible absorption of *Z*-**6** as well as using the measured extinction coefficient of *E*-**4** in acetonitrile ($\varepsilon_{358\ nm} = 25800\ M^{-1}\ cm^{-1}$, see SI Figure 4), the absorbance difference at the maximum can be related to a concentration of ca. 10^{-5} M. Normalizing to the total weight of silica gel (ca. 6 mg) and the amount of solvent used (3 mL), an approximate loading of 10^{-5} mol/g was estimated.

Spectroscopy

UV-visible absorption spectra were recorded using quartz cuvettes of 1 cm length on a Cary 50 spectrophotometer equipped with a Peltier-thermostated cell holder at 25 ± 0.05 °C. All solvents employed in optical spectroscopy studies were of spectrophotometric grade. Analytical irradiation experiments employing the immobilization precursor *E*-**4** (see SI Figure 1) were performed on solutions in CH_3CN using a LOT-Oriel 1000 W medium-pressure xenon lamp (XBO) equipped with two cut-off filters resulting in a narrow spectral window ($\lambda_{max\ T}$ = 365 nm @ 35% T, FWHM = 42 nm, correlating to approximately 4-5 $mW \cdot m^{-2} \cdot nm^{-1}$). For photochemical $Z \rightarrow E$ isomerization of *Z*-**4** a cut-off filter was used ($\lambda_{max} > 400$ nm @ T = 65%, correlating to approximately 12-13 $mW \cdot m^{-2} \cdot nm^{-1}$). Analytical irradiation experiments employing silica gel supported catalyst *E*-**6** (see MS Figure 3) were performed on suspensions of the material in methylene chloride (6.14 mg of *E*-**6** in 3 mL CH_2Cl_2). Lamp and filters were the same as reported for immobilization precursor *E*-**4**. Thermal $Z \rightarrow E$ isomerization of *Z*-**4** was monitored by UV/vis spectroscopy (see SI Figure 2). The rate constants of the thermal *Z*-**4** → *E*-**4** at different temperatures were obtained by plotting -ln([*Z*-**4**]) calculated from UV-vis spectra versus time (see insets in SI Figure 2). Activation parameters were determined by plotting ln (k/T) versus 1/T (van't Hoff plot, SI Figure 3 and SI Table 1). The quantitative UV/vis spectrum of *Z*-**4** was determined combining spectroscopy and chromatography data (see SI Figures 4).

pH-Measurements

pH-Measurements were conducted with a Schott pH-Meter CG 825 and a Mettler-Toledo InLab Micro pH-electrode calibrated with buffers at pH = 4 and pH = 7. Suspensions of silica gel (Acros, 130 - 400 mesh) and silica gel supported catalyst **6** in the two switching states (*E*-isomer and PSS) were measured in a thermostated shaker at 20 °C using Millipore® water as solvent. Results of the measurements are summarized in SI Table 2. In addition, the switching process of the supported catalyst **6** was followed in water (see SI Figure 5).

Figures & Table

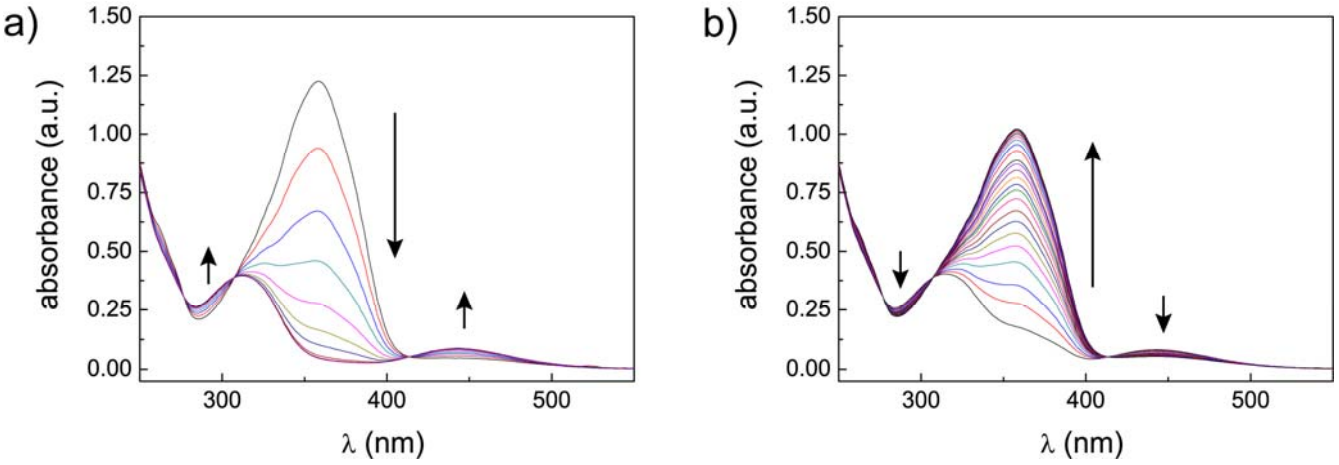


Figure 1. Irradiation of immobilization precursor **4**: a) isomerization *E*-**4** → *Z*-**4** (365 nm, 2 min 30 s irradiation time, 4.76 · 10^{-5} M in CH_3CN); b) isomerization *Z*-**4** → *E*-**4** (400 nm, 5 min, 4.76 · 10^{-5} M in CH_3CN).

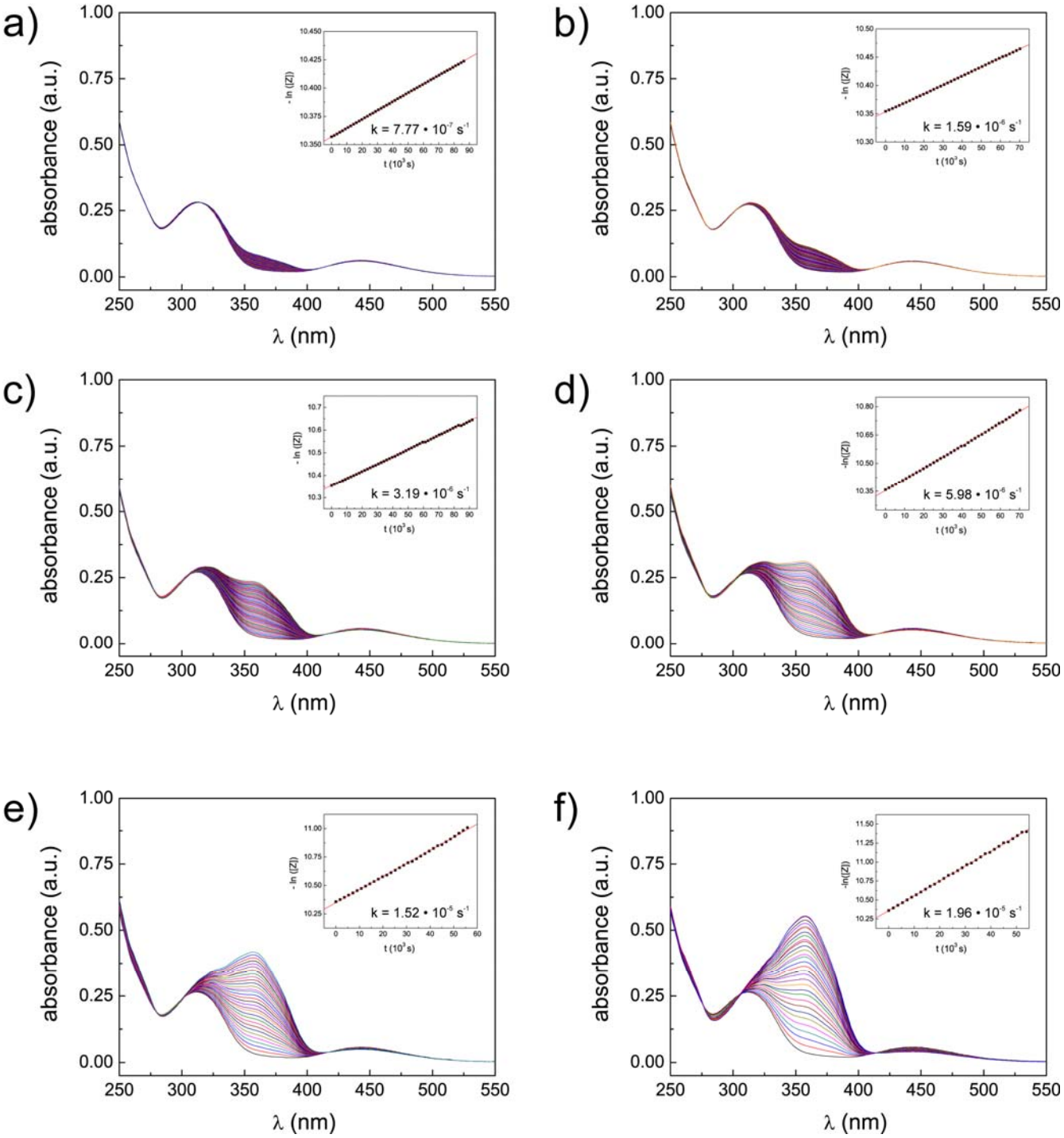


Figure 2. Thermal isomerization of *Z*-**4** → *E*-**4** at varying temperatures; insets show plots of -ln([*Z*]) vs. time and derived rate constants. a) 20 °C for 24 h ($3.24 \cdot 10^{-5}$ M in CH_3CN), b) 25 °C for 19.5 h ($3.24 \cdot 10^{-5}$ M in CH_3CN), c) 30 °C for 25.5 h ($3.24 \cdot 10^{-5}$ M in CH_3CN), d) 35 °C for 19.5 h ($3.24 \cdot 10^{-5}$ M in CH_3CN), e) 40 °C for 15.5 h ($3.24 \cdot 10^{-5}$ M in CH_3CN), f) 45 °C for 15 h ($3.24 \cdot 10^{-5}$ M in CH_3CN).

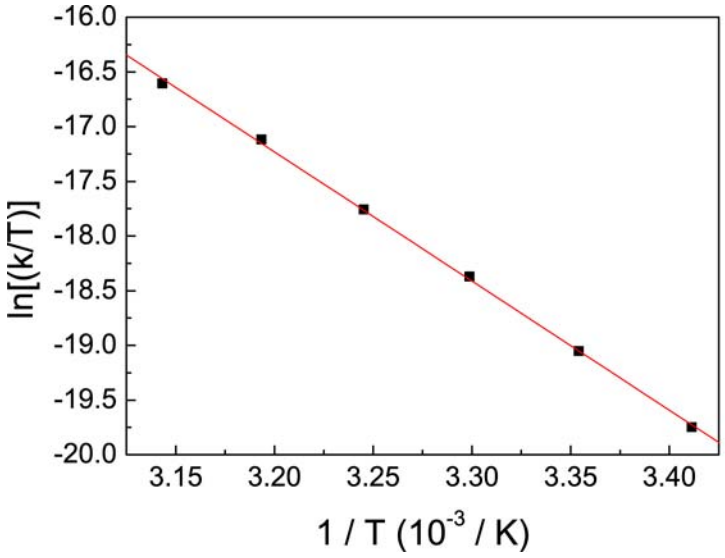


Figure 3. Van't Hoff plot for thermal $Z \rightarrow E$ isomerization of **4** obtained by plotting ln(k/T) versus 1/T. Obtained activation parameters are given in SI Table.

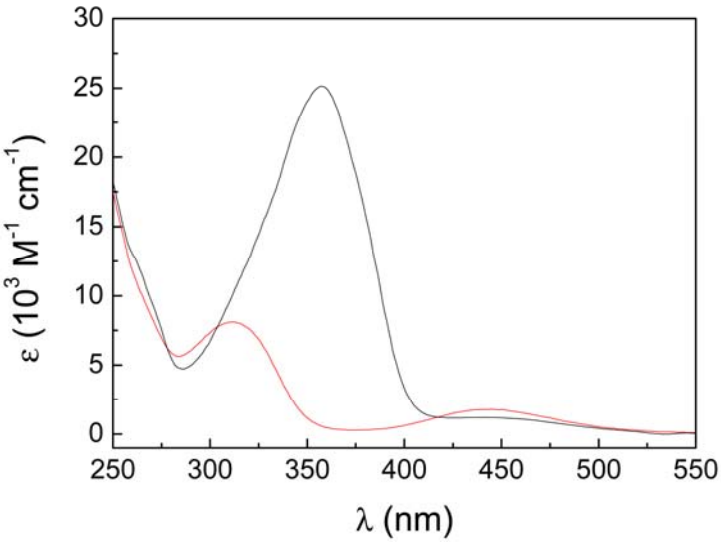


Figure 4. UV/vis-spectra of *E*-**4** (black, c = $3.2 \cdot 10^{-5}$ M, $\varepsilon_{358\,nm} = 25800\ M^{-1}\,cm^{-1}$) and *Z*-**4** (red, c = $3.2 \cdot 10^{-5}$ M, $\varepsilon_{312\,nm} = 800\ M^{-1}\,cm^{-1}$) in CH_3CN. The spectrum of *Z*-**4** was calculated from the UV/vis spectra of pure *E*-**4** and the *E* : *Z* mixture at the photostationary state, for which the *E* : *Z* ratio was determined by UPLC separation.

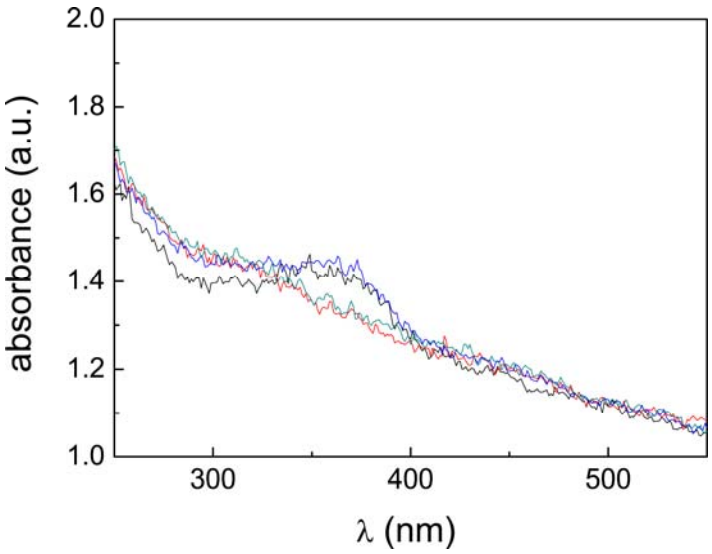


Figure 5. Irradiation of silica gel supported catalyst **6** (6.24 mg in 3 mL of Millipore® water; black: *E* isomer, dark sample; red: $PSS_{E \rightarrow Z}$, 2.5 min irradiation time, 365 nm; blue: $PSS_{Z \rightarrow E}$, 1 min irradiation time, 400 nm; cyan: $PSS_{E \rightarrow Z}$, 2.5 min irradiation time, 365 nm, 2nd irradiation).

Table 1. Summary of photochromic properties and activation parameters for thermal $Z \rightarrow E$ isomerization of **4**.

	absorption		PSS composition	
	$\lambda_{max}(E)$[a] [nm]	$\lambda_{max}(Z)$[b] [nm]	$E \rightarrow Z$ (Z/E)	$Z \rightarrow E$ (Z/E)
4	358	443	98:2	77:23
	thermal $Z \rightarrow E$ isomerization			
	$\tau_{1/2}$[c] [h]	$\Delta G^{\ddagger}_{298\,K}$[d] [kcal mol^{-1}]	$\Delta H^{\ddagger}$[d] [kcal mol^{-1}]	$\Delta S^{\ddagger}$[d] [cal mol^{-1} K^{-1}]
4	248	25	23	-6

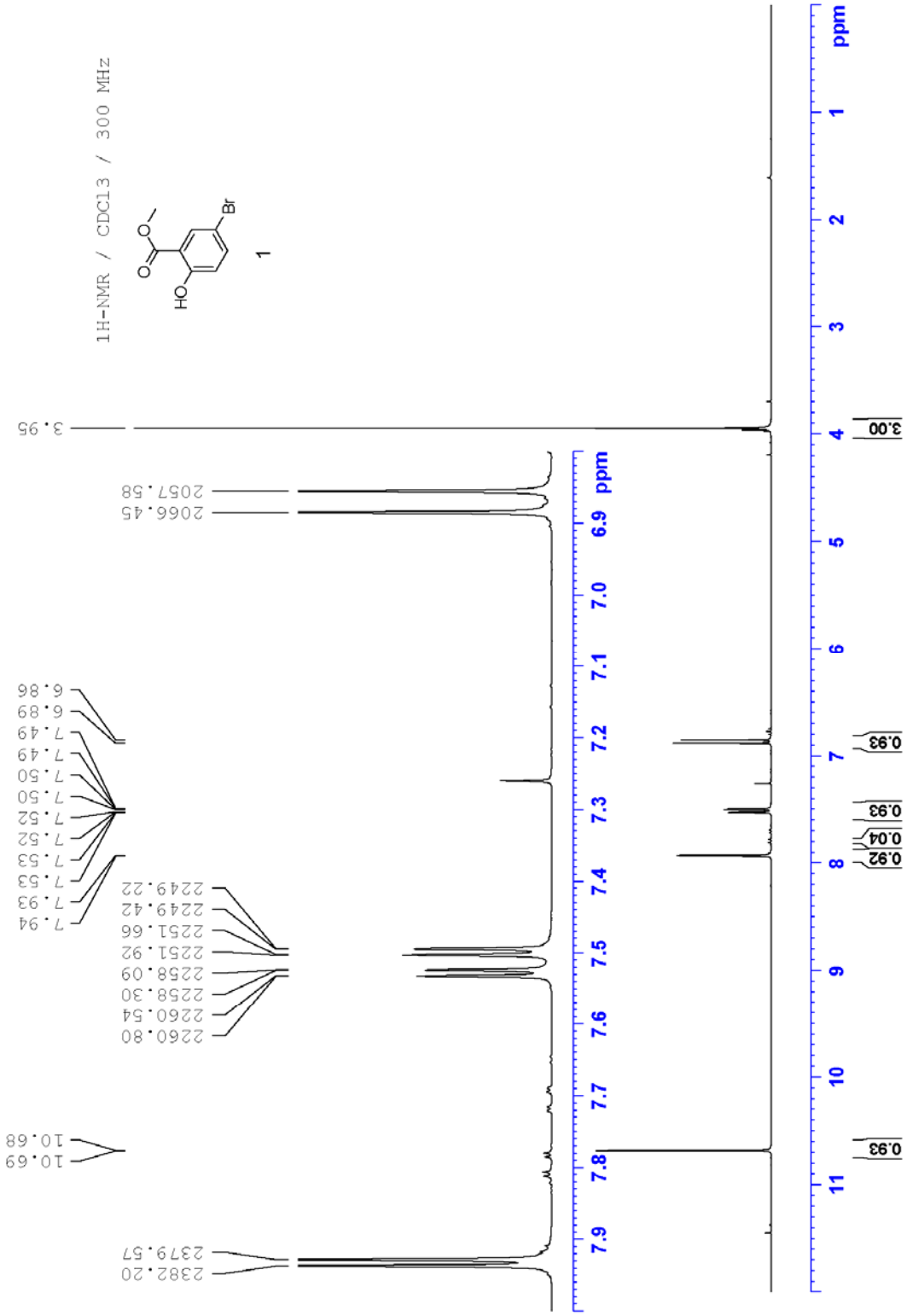
[a] π,π*-Absorption. [b] n,π*-Absorption. [c] At 20 °C (293.15 K). [d] Obtained from kinetic data of the thermal $Z \rightarrow E$ isomerization at various temperatures and Eyring analysis of the data.

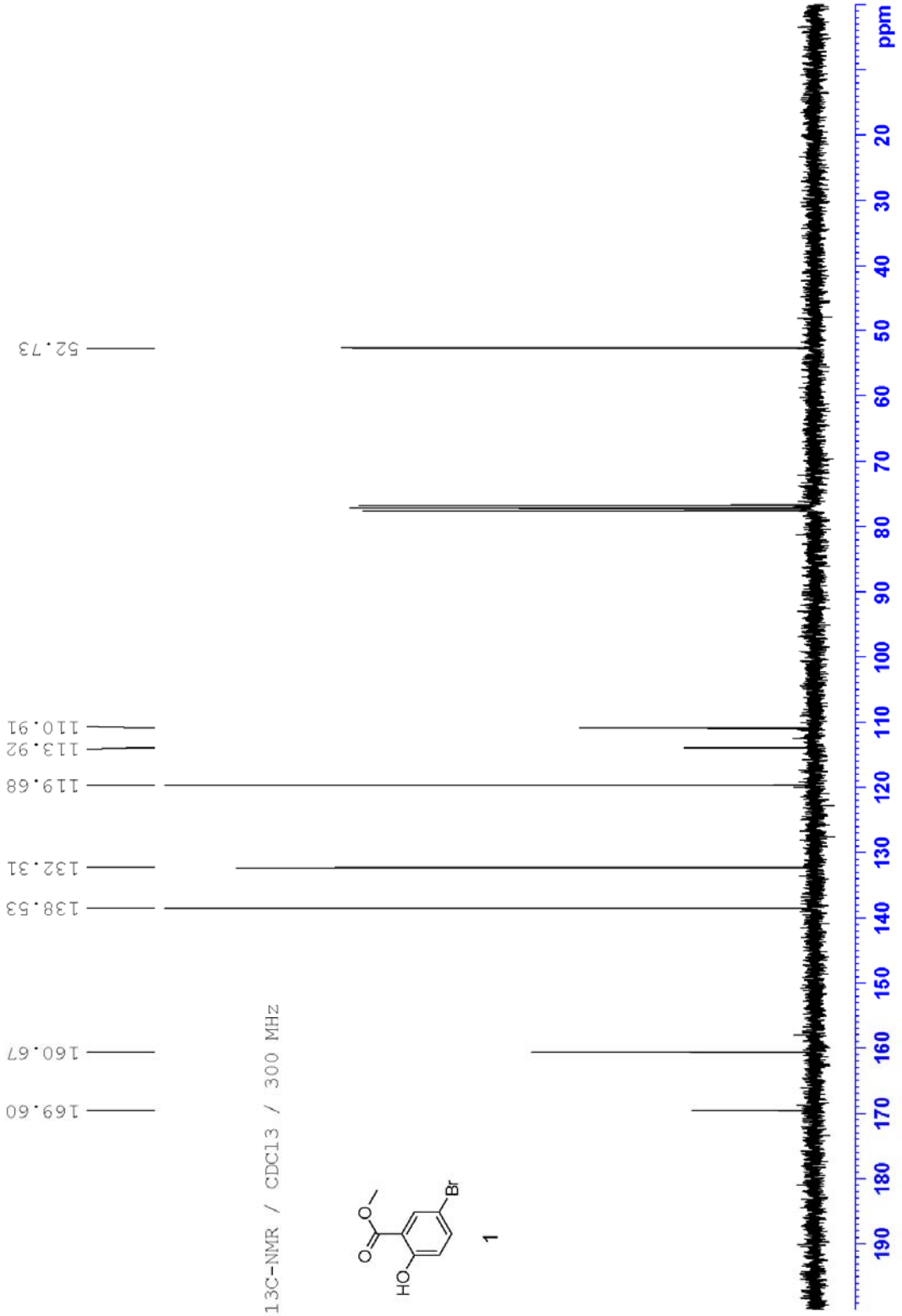
Table 2. Summary of pH-measurements of silica gel and silica gel supported catalyst **6** in 3 mL of Millipore® water at 20 °C.

sample	m (silica gel) [mg]	switching state	pH
Millipore® water	-	-	7.00
silica gel	6.01	-	6.81
supported catalyst **6**	6.26	*E*	6.63
		$PSS_{Z \rightarrow E}$[a]	6.89

[a] Obtained after 5 min irradiation using a LOT-Oriel 1000W medium-pressure xenon lamp (XBO) equipped with two cut-off filters resulting in a narrow spectral window ($\lambda_{max\,T}$ = 365 nm @ 35% T, FWHM = 42 nm).

Copies of NMR Spectra

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138.53
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O
HO
Br
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ppm
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110
120
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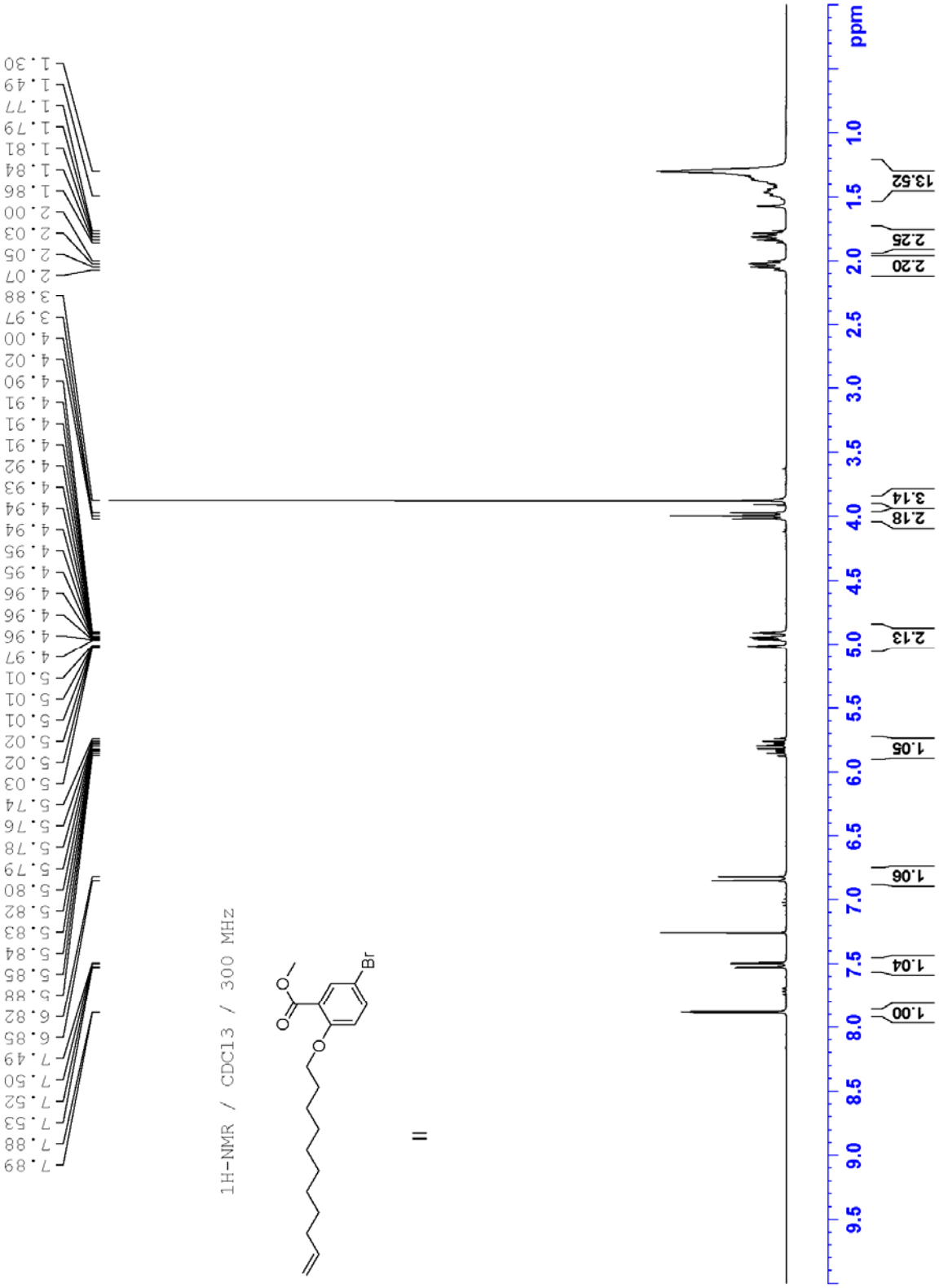
150
160
170
180
190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O
=
ppm
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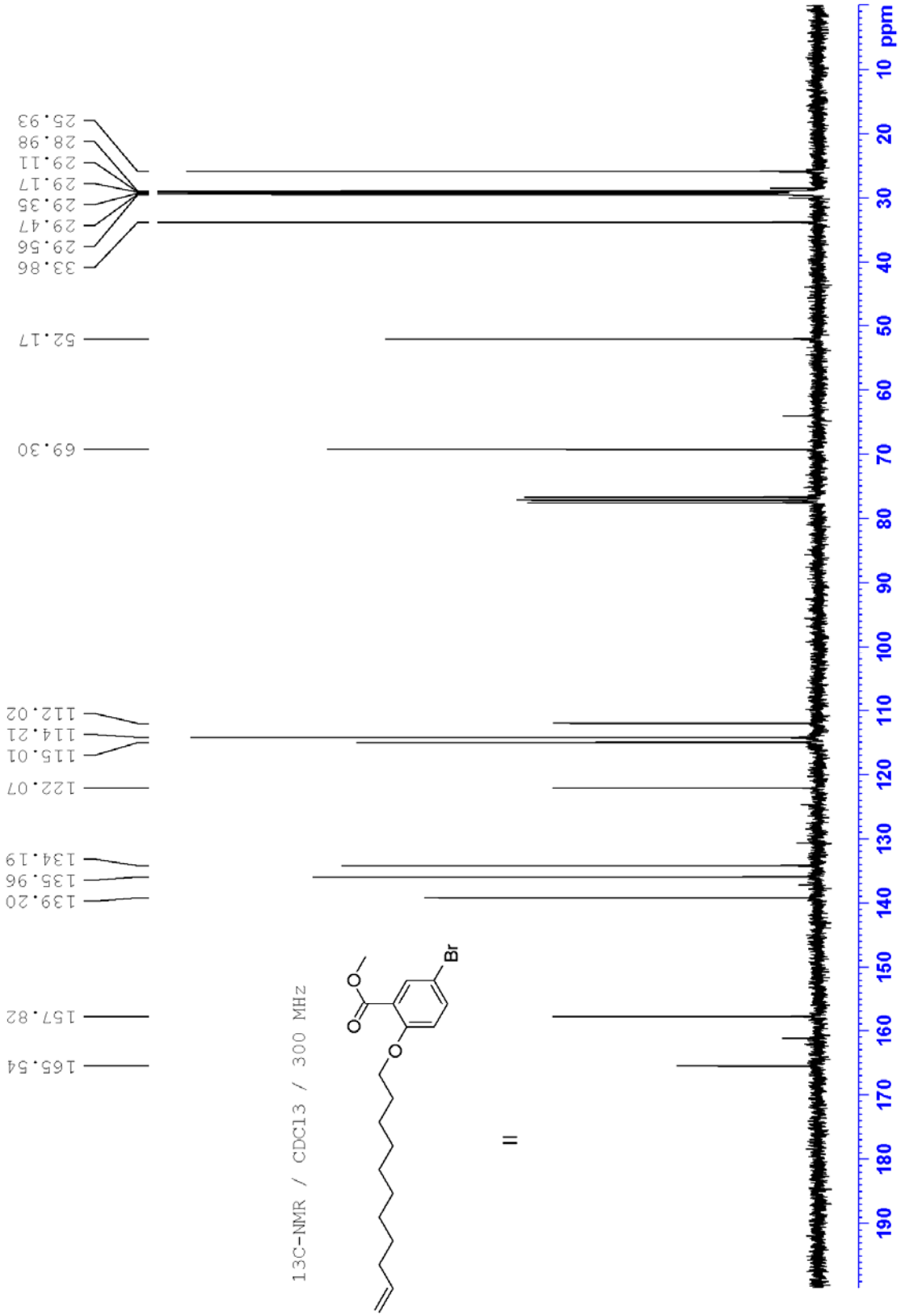
1.00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33.86
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115.01
122.07
134.19
135.96
139.20
157.82
165.54
13C-NMR / CDCl3 / 300 MHz
Br
O
O
O
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40
50
60
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100
110
120
130
140
150
160
170
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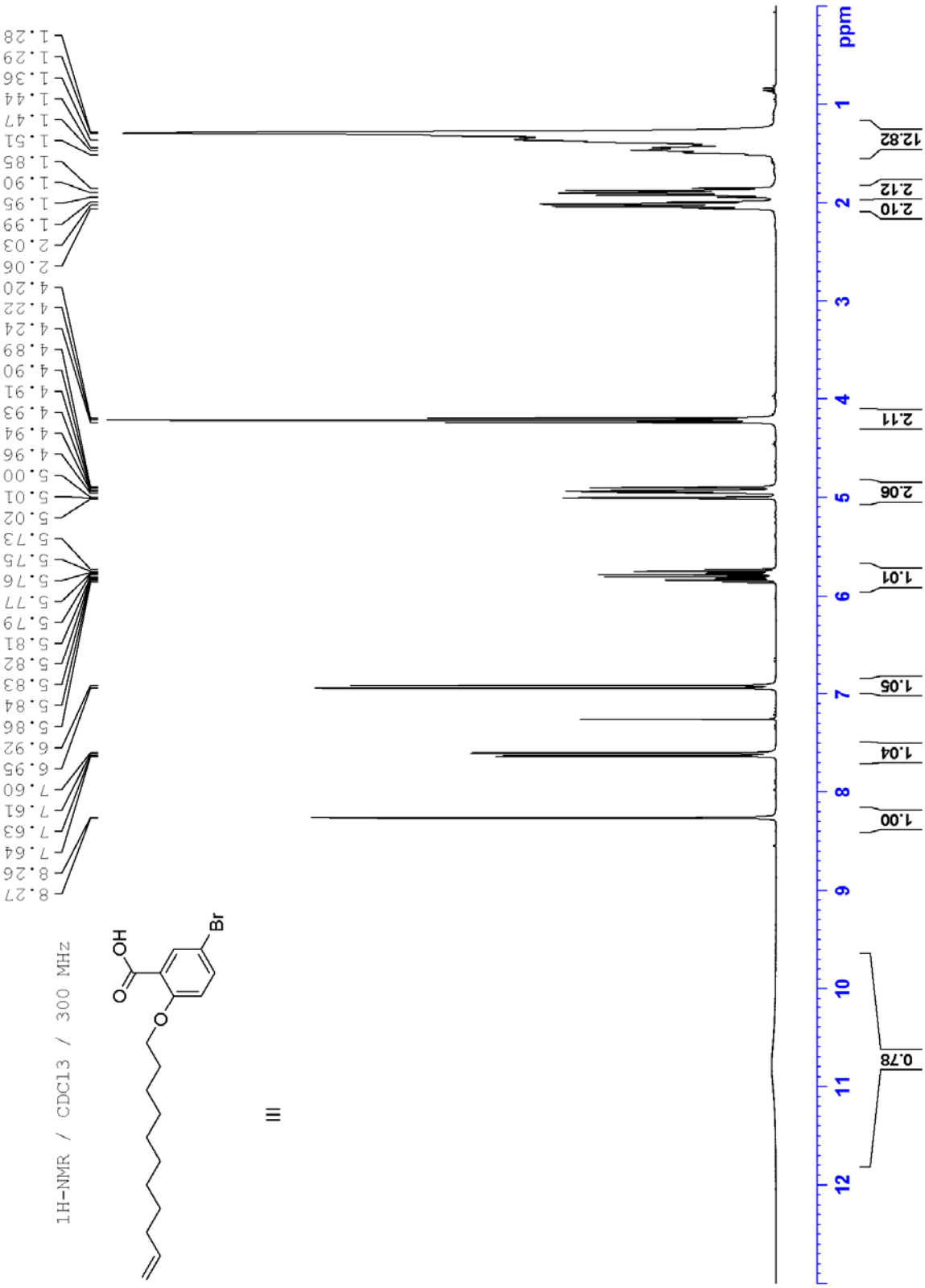
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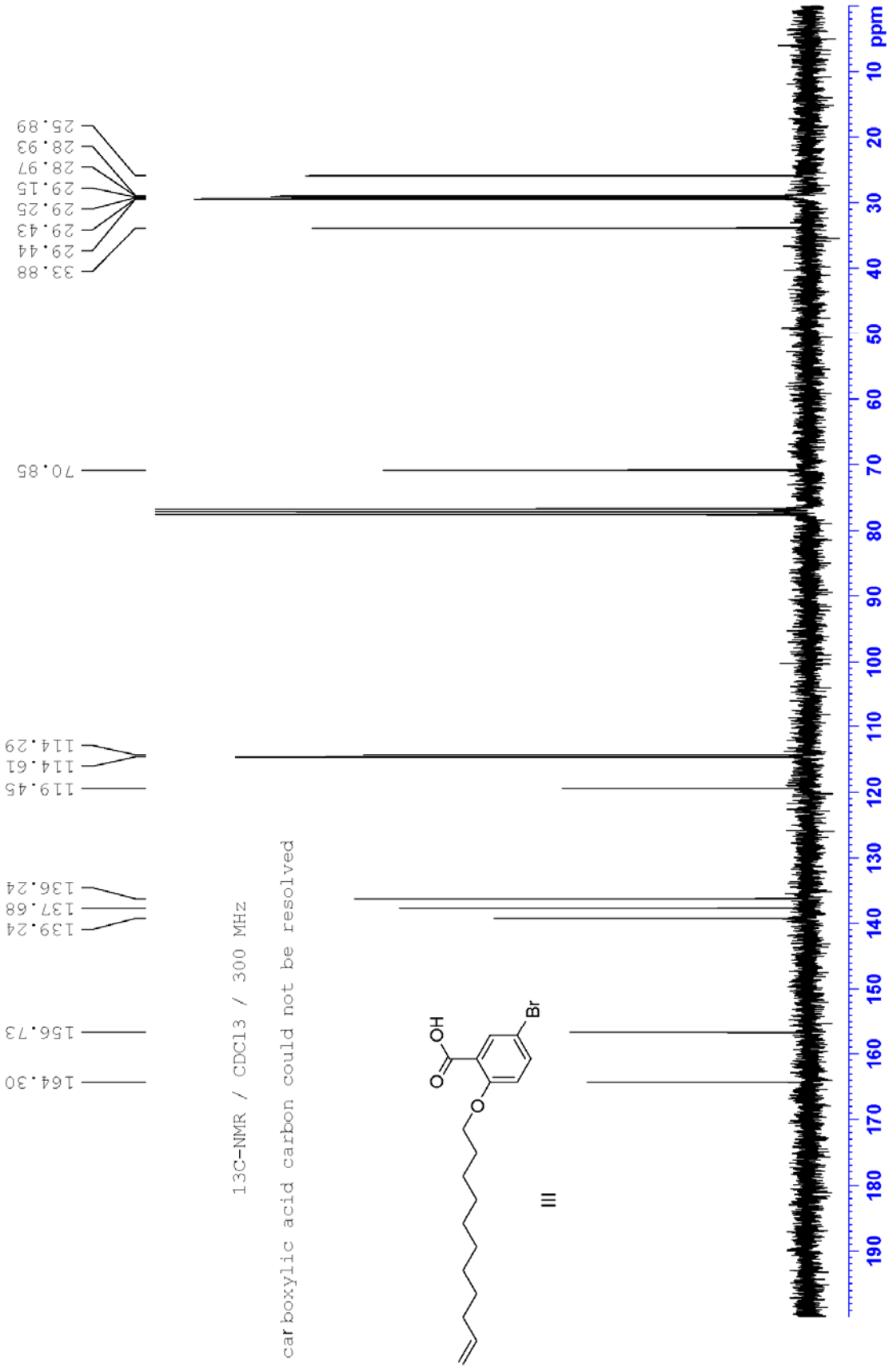
O
O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180
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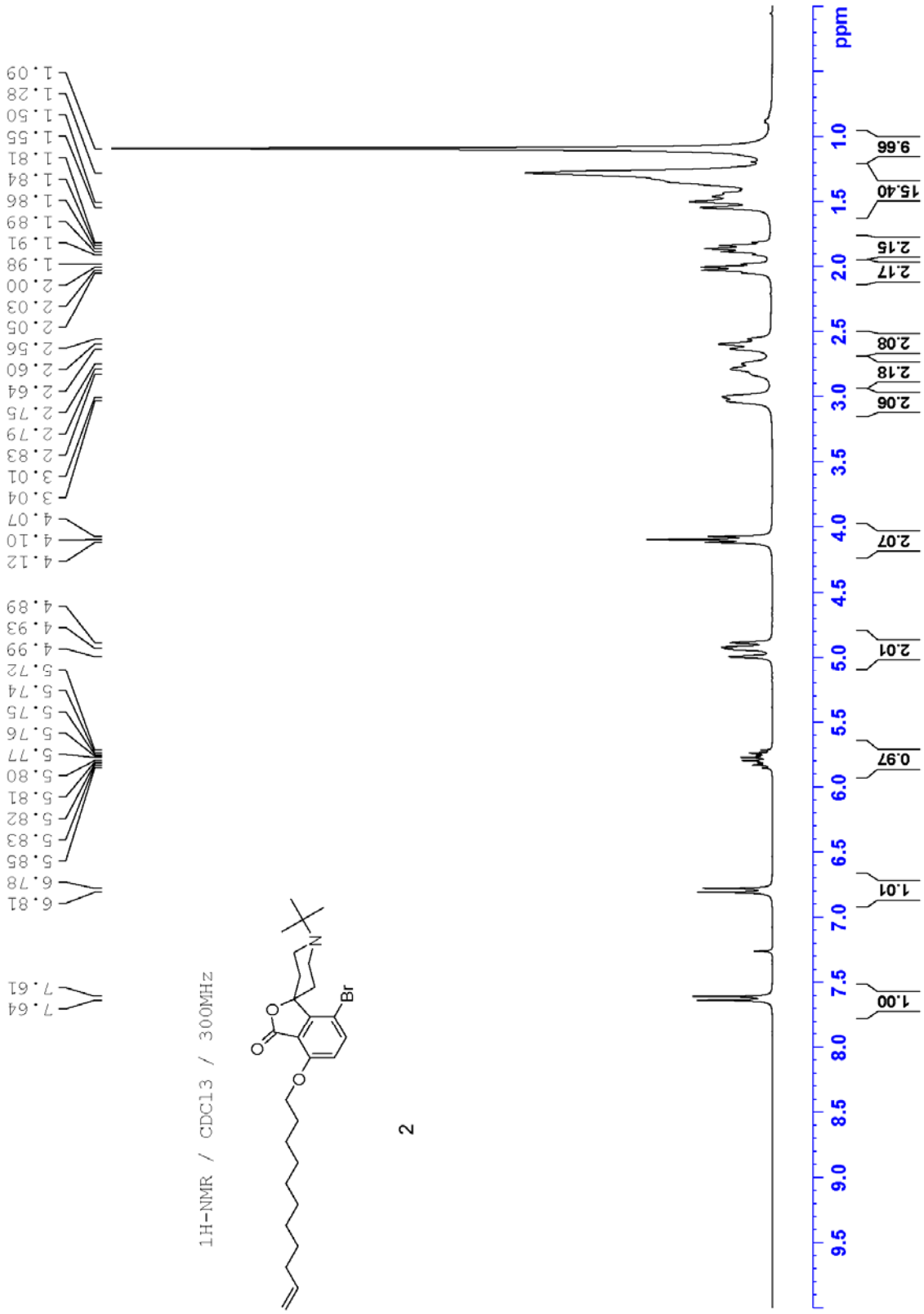
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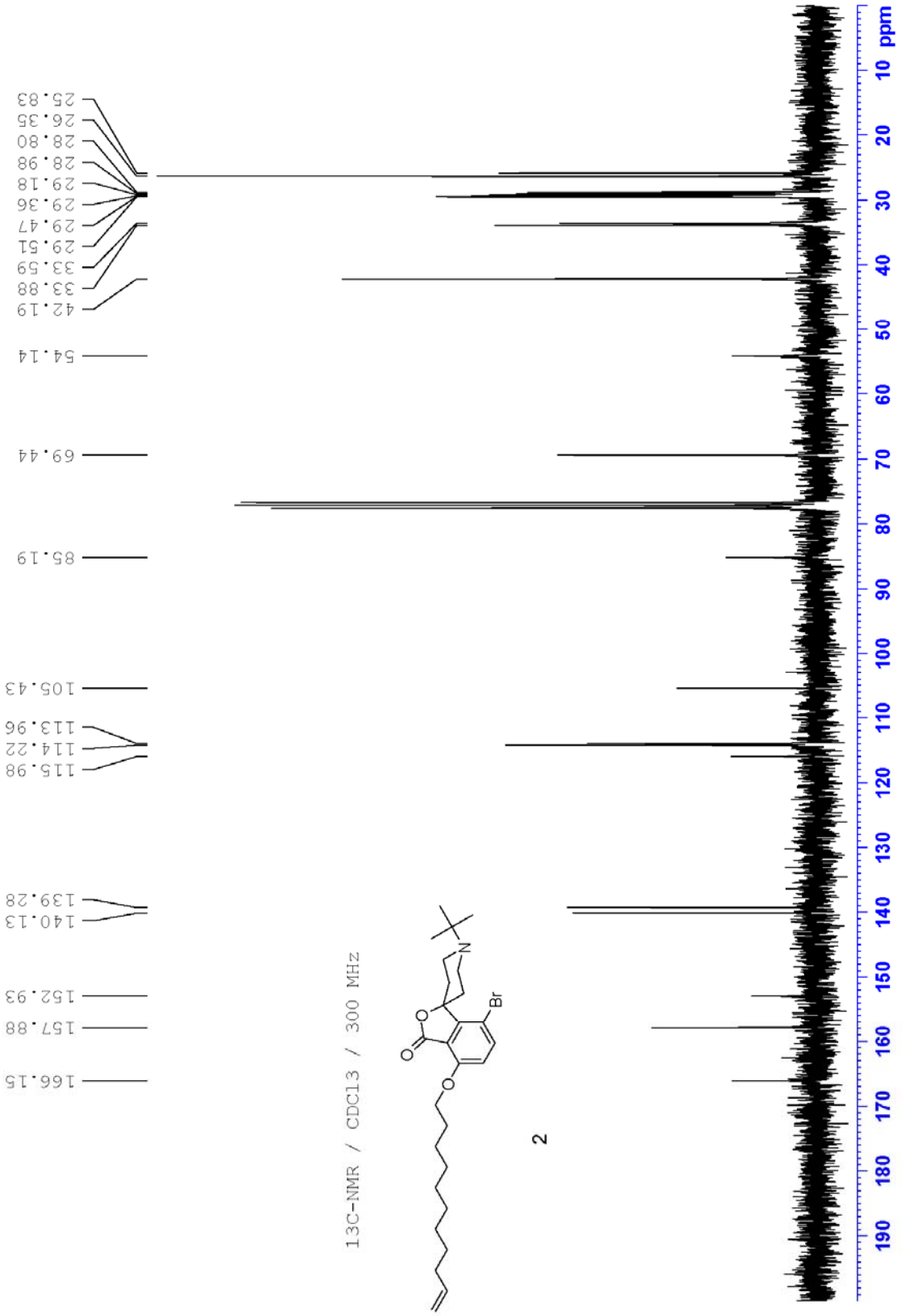
1.00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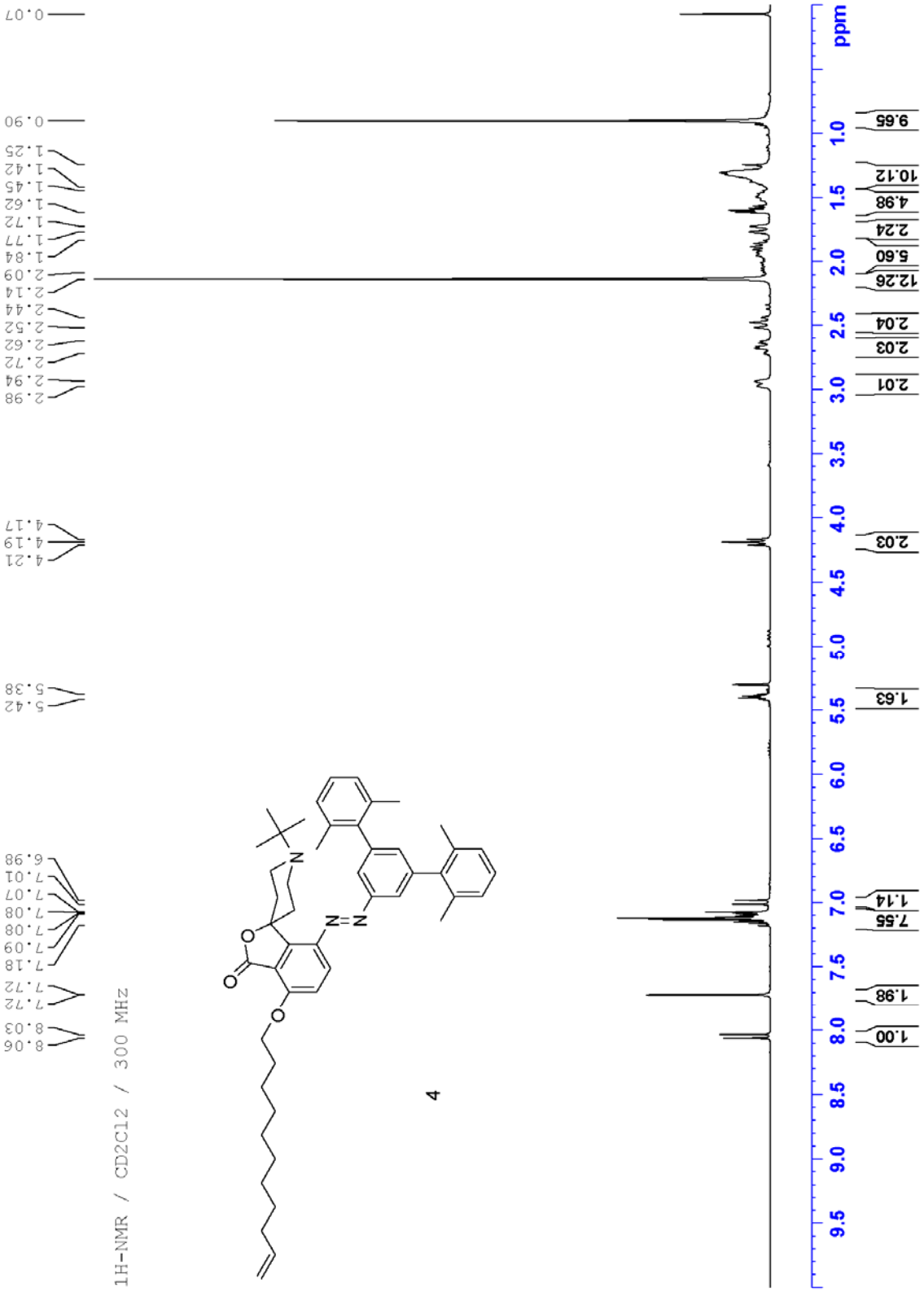
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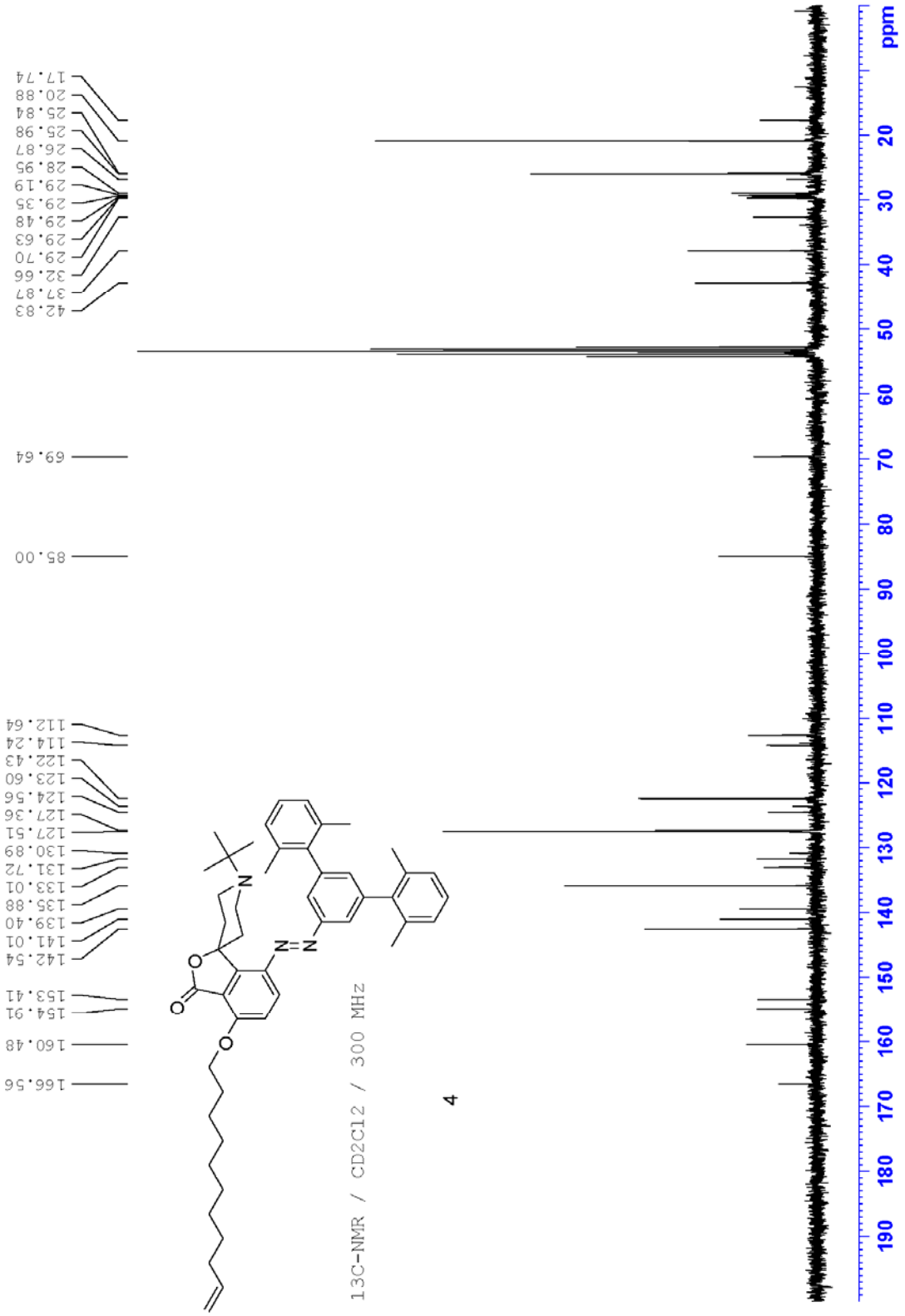
ppm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37.87
42.83
69.64
85.00
112.64
114.24
122.43
123.60
124.56
127.36
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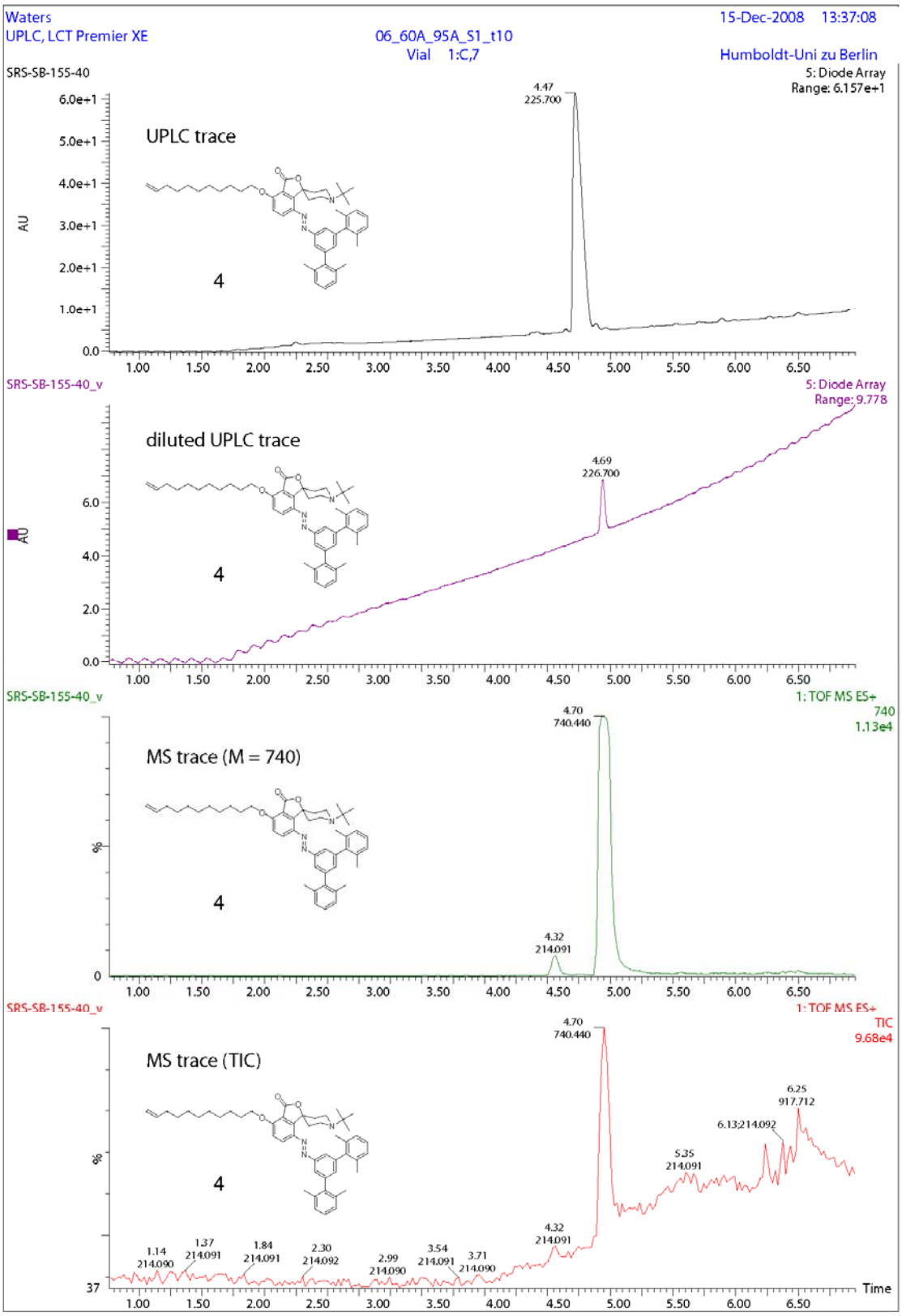
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225.700
AU
4
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5: Diode Array
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diluted UPLC trace
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