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Supporting Information

Low Molecular Weight Norbornadiene Derivatives for Molecular Solar-Thermal Energy Storage

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Supporting Information

Contents

S.1 NMR Spectroscopy

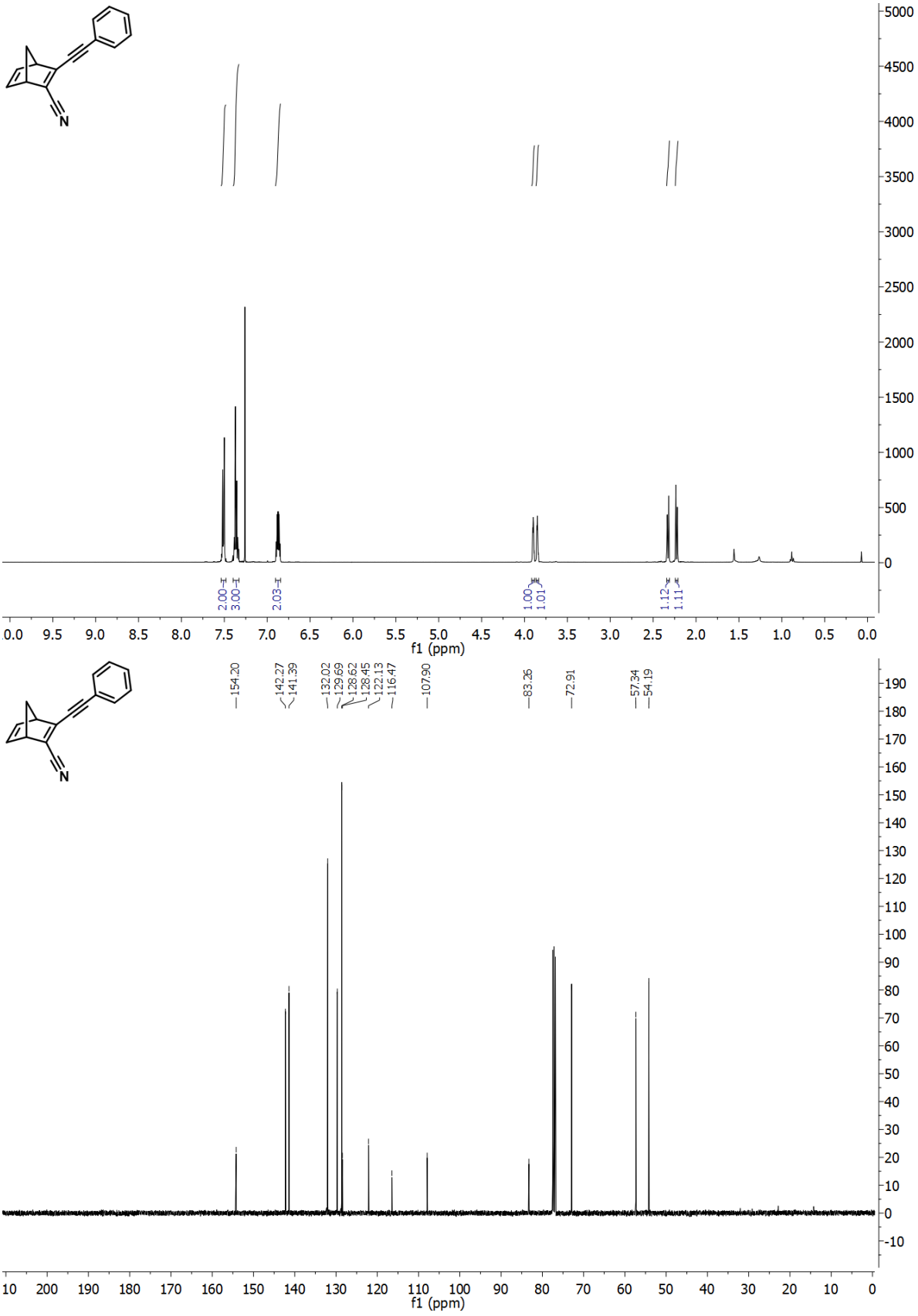


Figure S1.1. ^{1}H- and ^{13}C-NMR for **4a**.

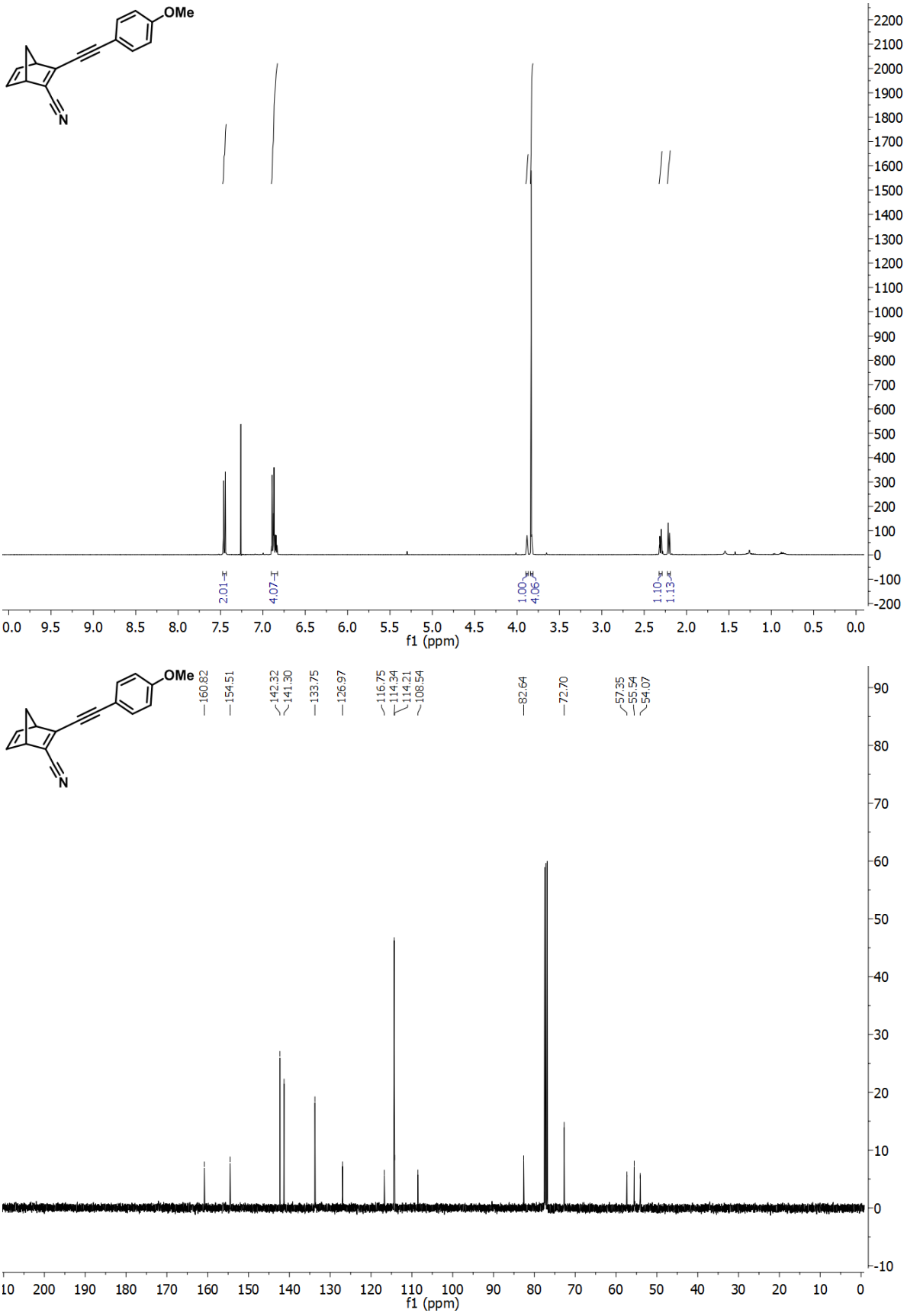


Figure S1.2. ^{1}H- and ^{13}C-NMR for **4b**.

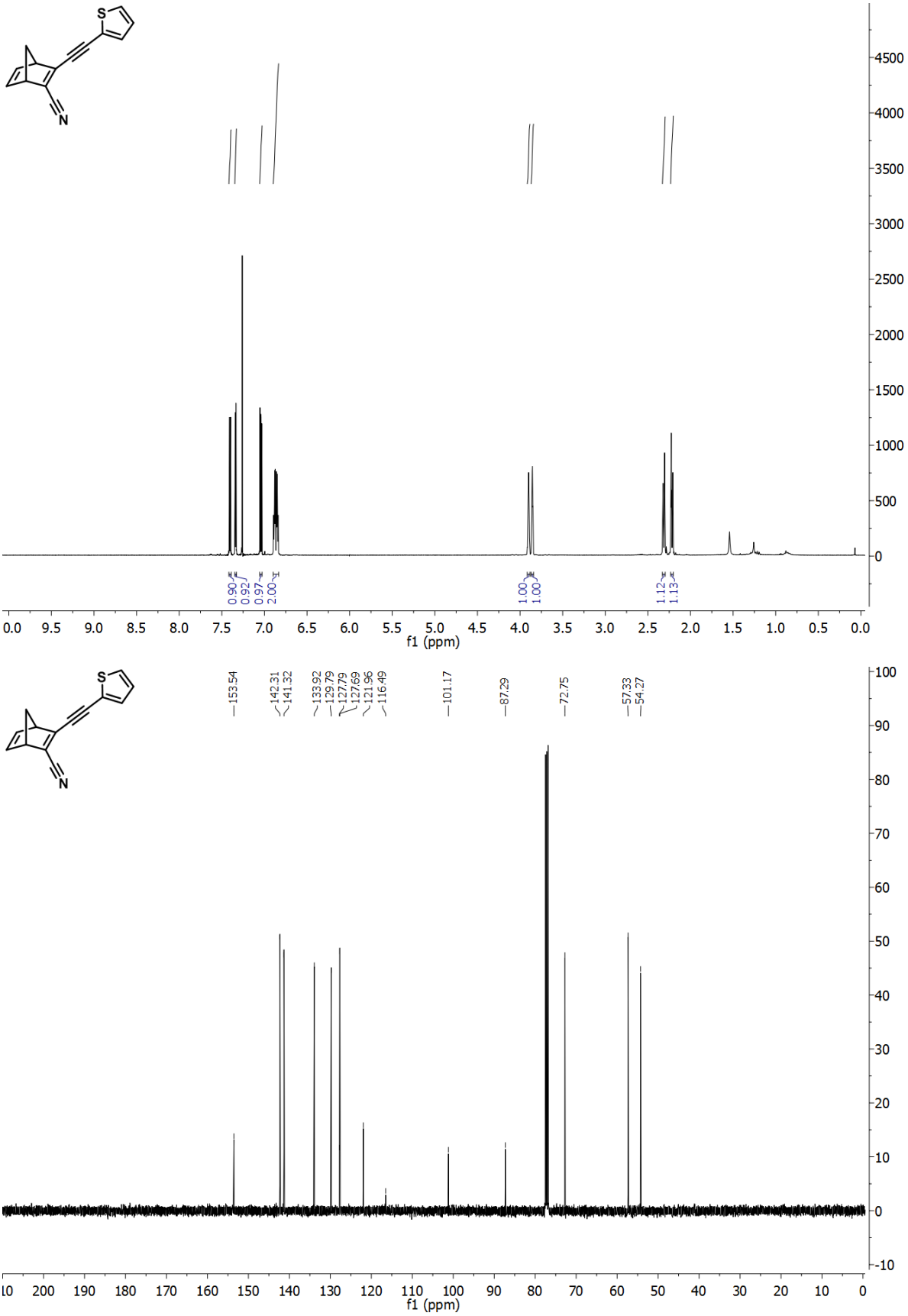


Figure S1.3. ^{1}H- and ^{13}C-NMR for **4c**.

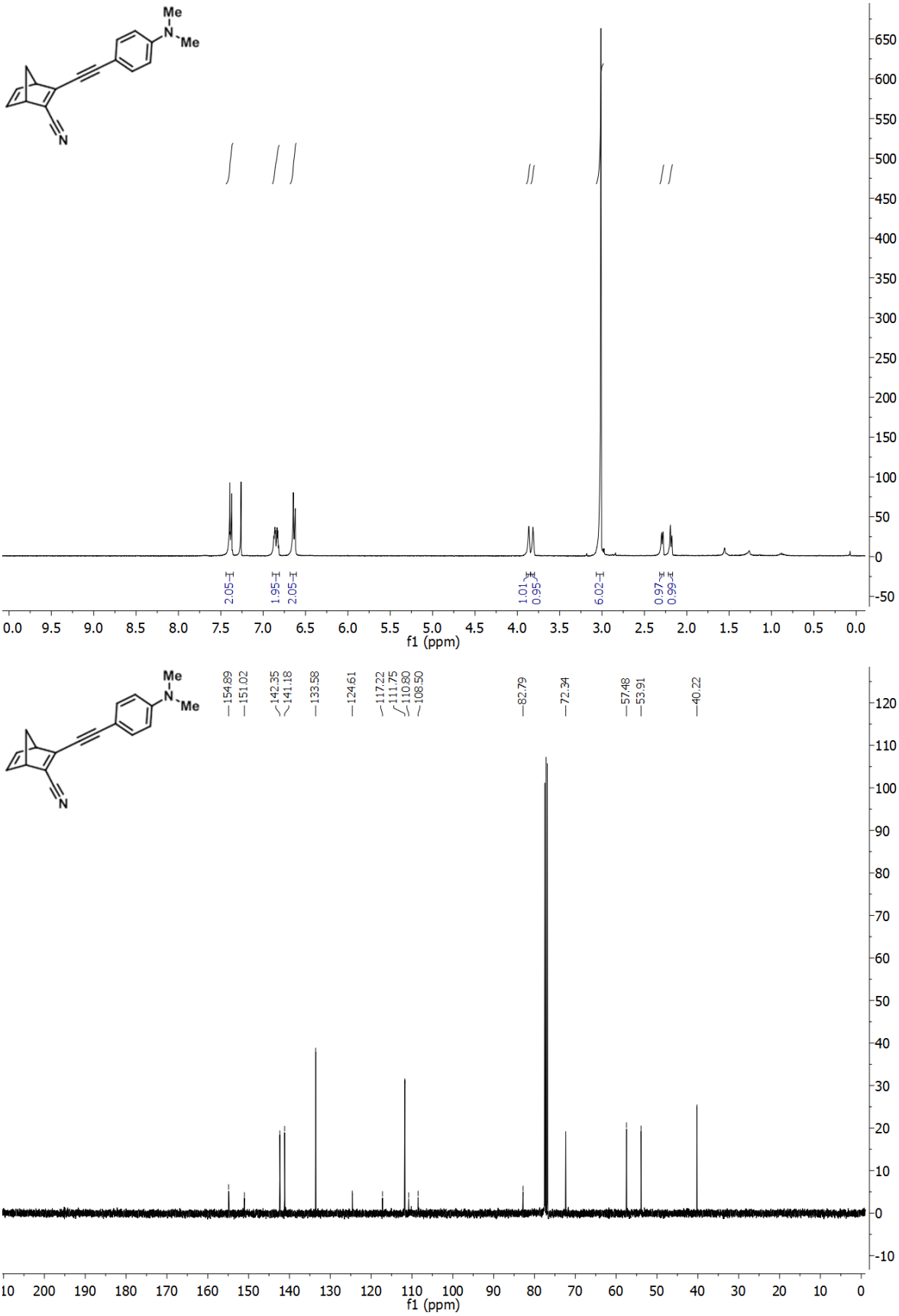


Figure S1.4. ^{1}H- and ^{13}C-NMR for **4d**.

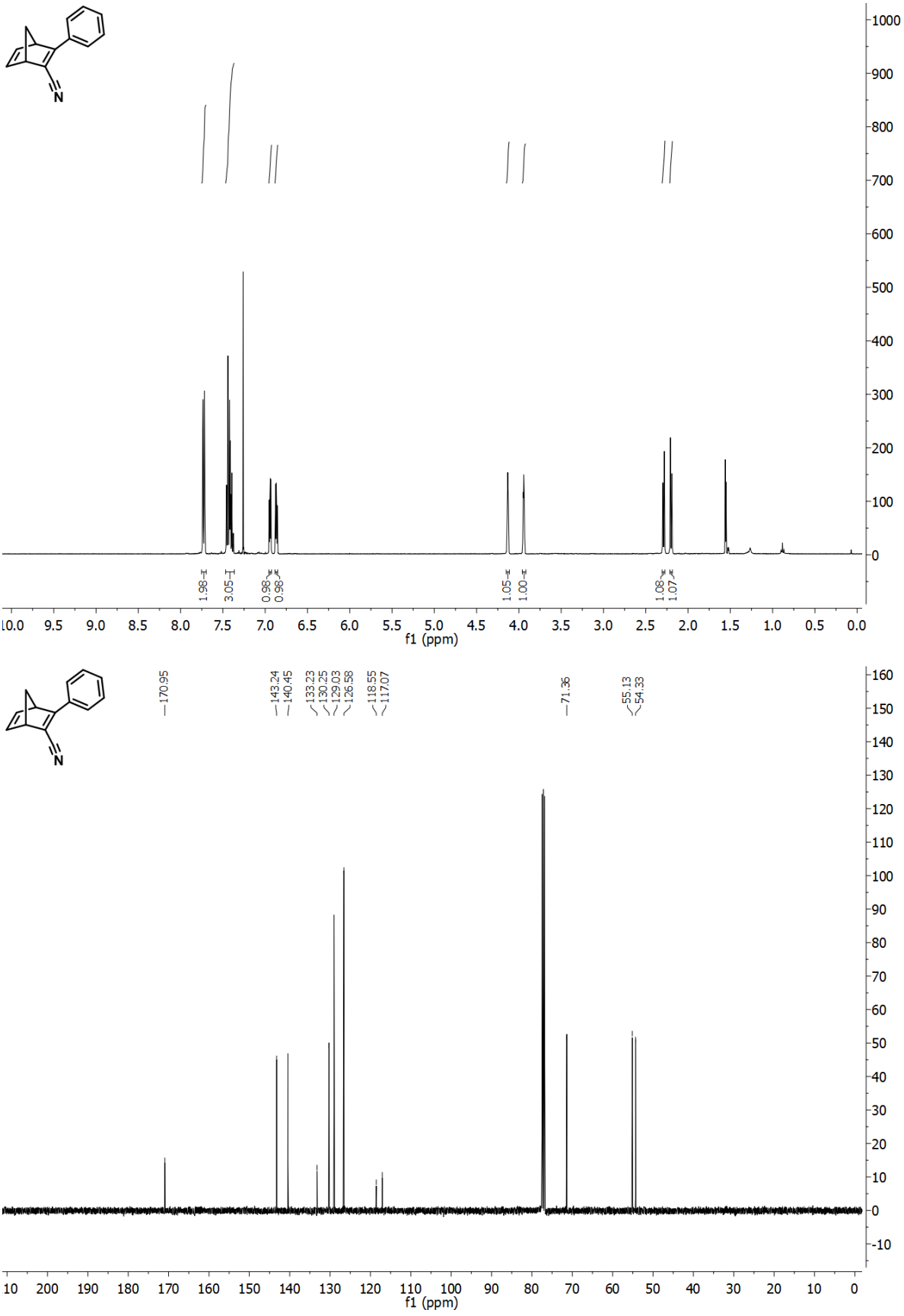


Figure S1.5. ^{1}H- and ^{13}C-NMR for **5**.

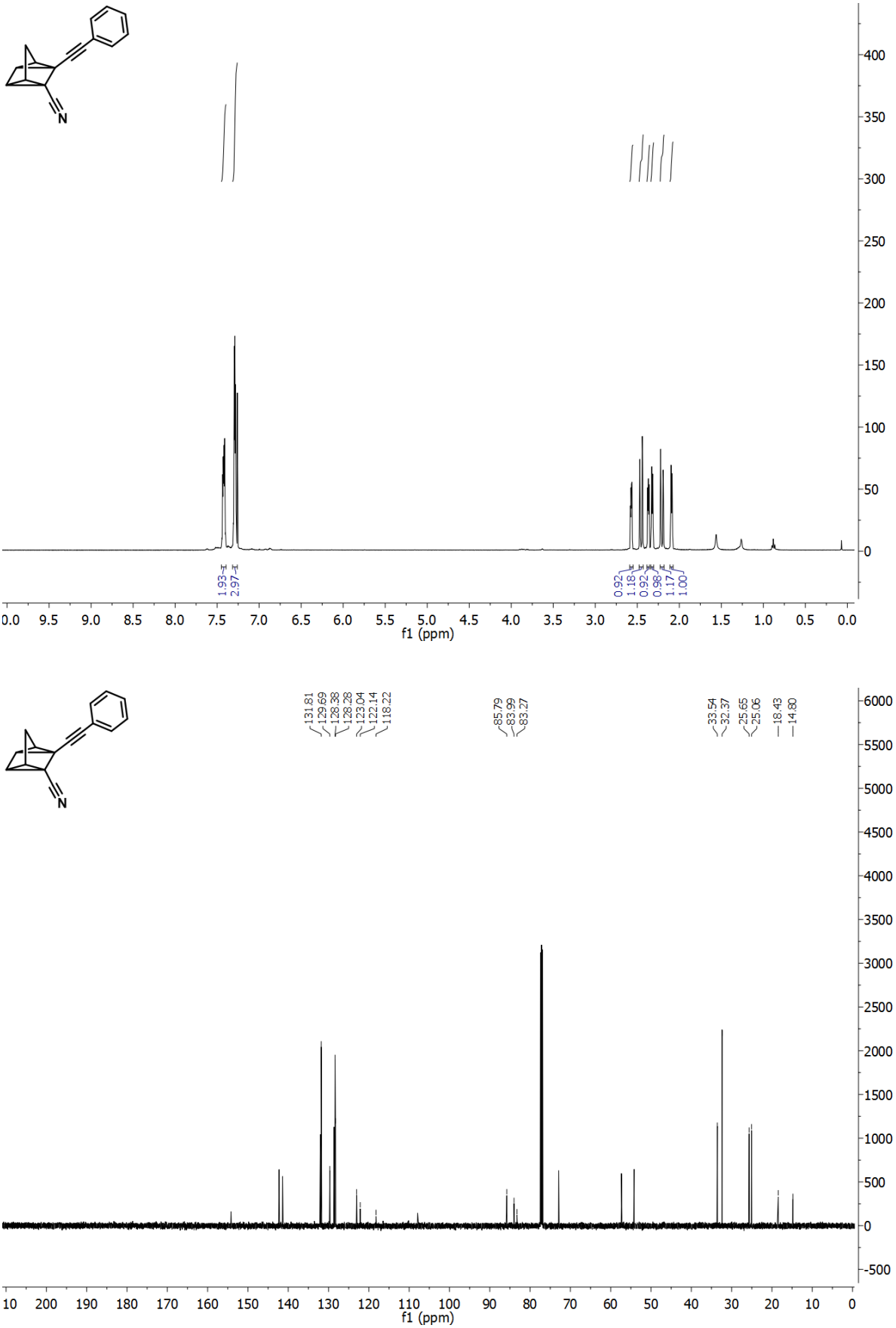


Figure S1.6. ^{1}H- and ^{13}C-NMR for **15a**. ^{13}C-NMR was recorded on a Varian 500 MHz, due to fast backconversion peaks from **4a** is present in the spectra.

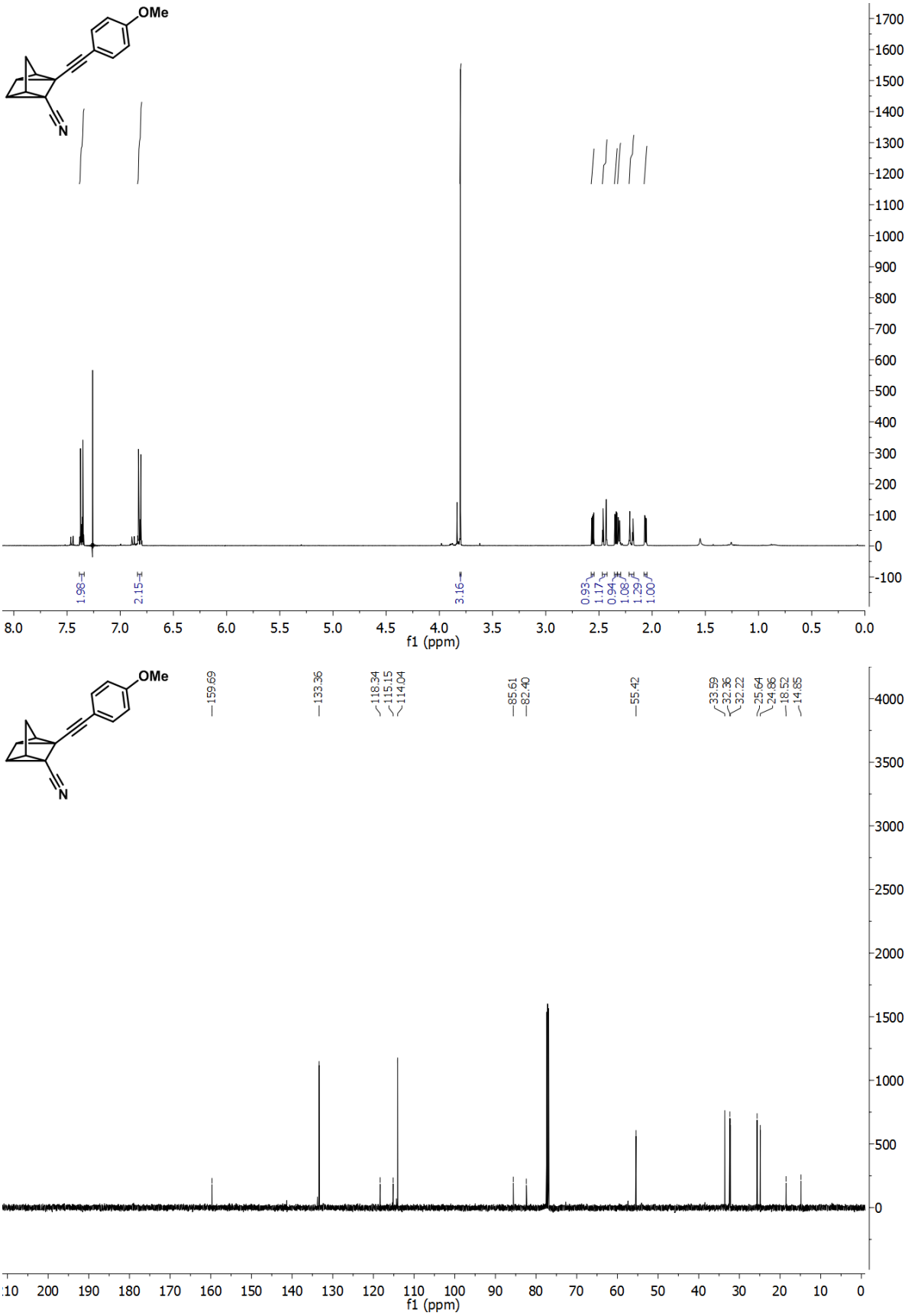


Figure S1.7. ^{1}H- and ^{13}C-NMR for **15b**. ^{13}C-NMR was recorded on a Varian 500 MHz.

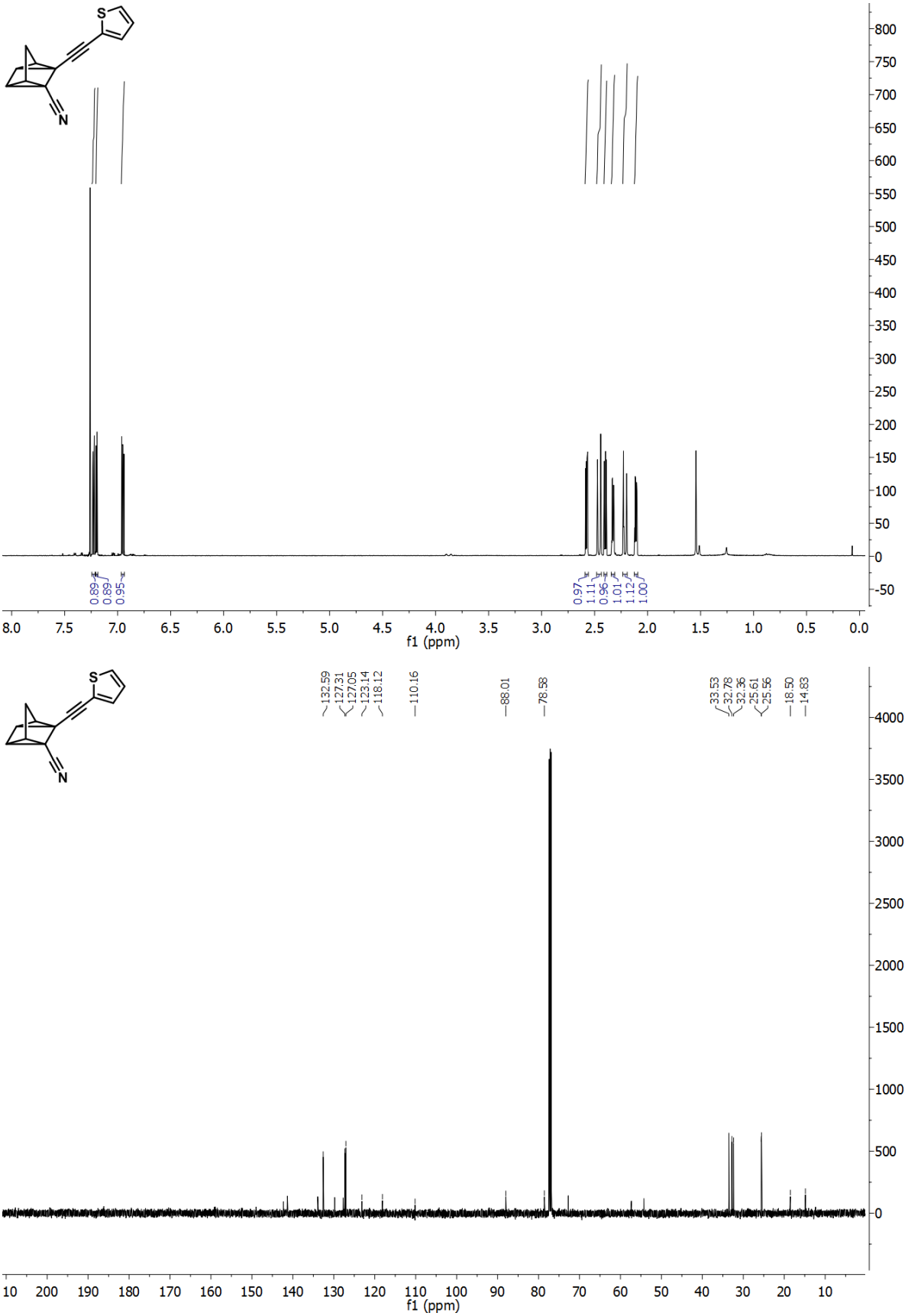


Figure S1.8. ^{1}H- and ^{13}C-NMR for **15c**. ^{13}C-NMR was recorded on a Varian 500 MHz, due to fast backconversion peaks from **4c** is present in the spectra.

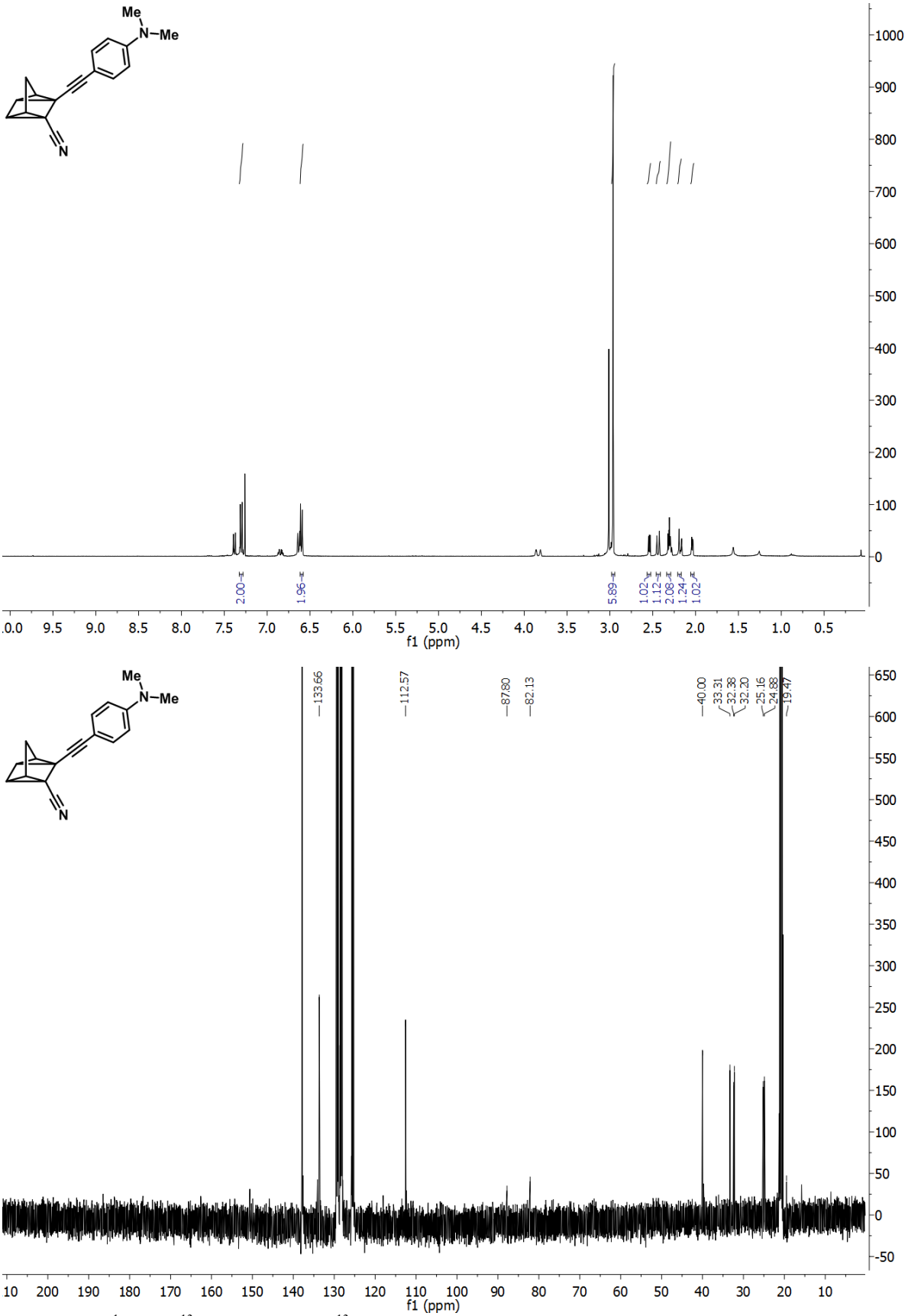


Figure S1.9. ^{1}H- and ^{13}C-NMR for **15d**. ^{13}C-NMR spectra was recorded on a Varian 500 MHz in toluene-*d*8. Due to fast backconversion peaks all carbon peaks were not recorded.

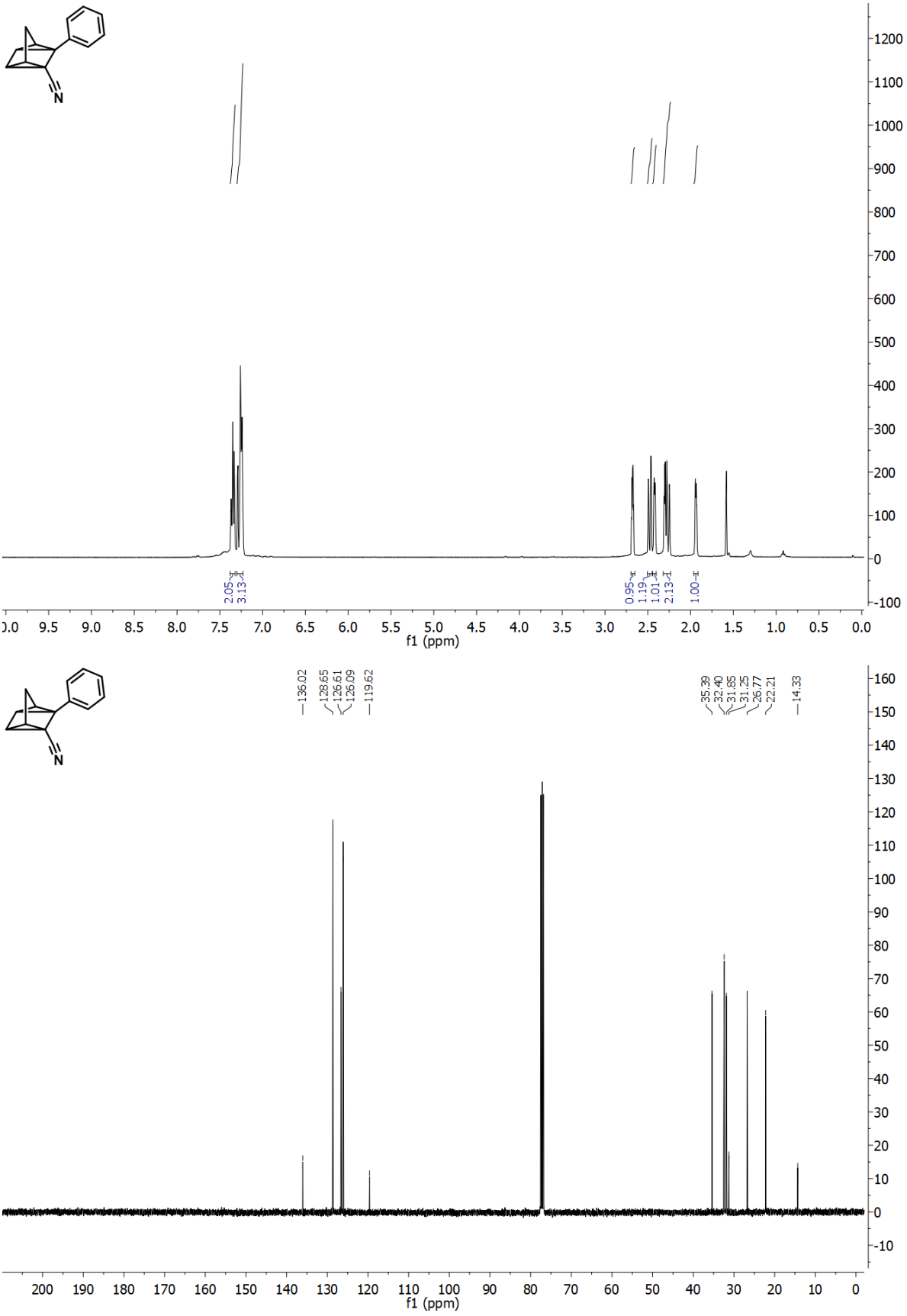


Figure S1.10. ^{1}H- and ^{13}C-NMR for **17.**

S.2 Quantum Yield Measurements

The photonflux of the irradiation source was determined by potassium ferrioxalate actinometry before and after the measurements were performed.[1] A fiber-coupled LED (M365F1 (365 nm)) was used as irradation source for **4b**, **4c** and **4d** and a fiber-coupled LED (M310L3 (310 nm)) for **4a** and **5**. The quantum yield measurments were carried out by irradiating a solution of norbornadiene in toulene and monitoring the decrease in absorption with a Cary 100 -UV-Visible spectrophotometer. The norbornadiene solutions were prepared and stored in the dark to avoid that any photoconversion occurred before measuremnts were executed. To ensure that all photons were absorbed, the concentration of the solutions were prepered to be optically thick at the irradiation wavelenght (absorption over 2, at 365 nm for **4b**, **4c** and **4d** and at 310 nm for **4a** and **5**).When all photons are absorbed, a linear dependence between the decrease in absorption and the irradiation time is obtained and the quantum yield can be determined from the slope.

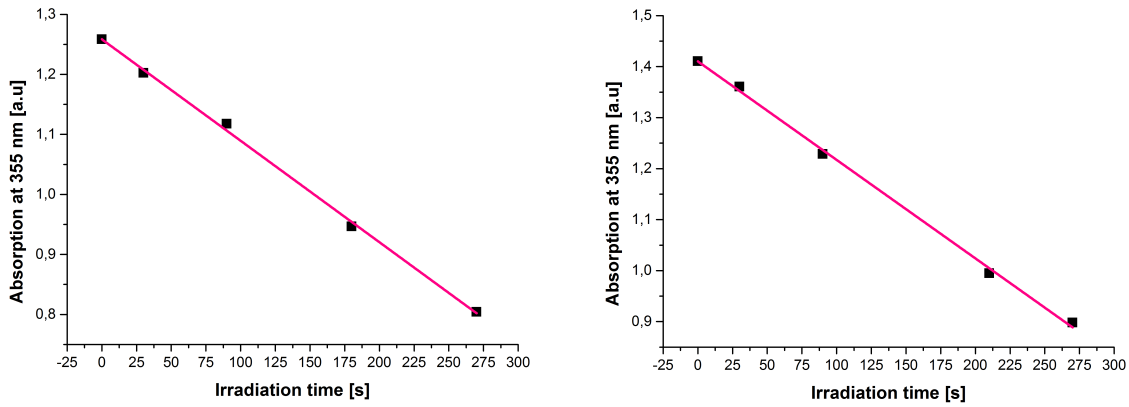


Figure S2.1. Absorption at 355 nm versus the irradiation time for the quantum yield measurements of the conversion of **4a** to **16a**. Experimental data is presented as squares and the line represents the linear fit.

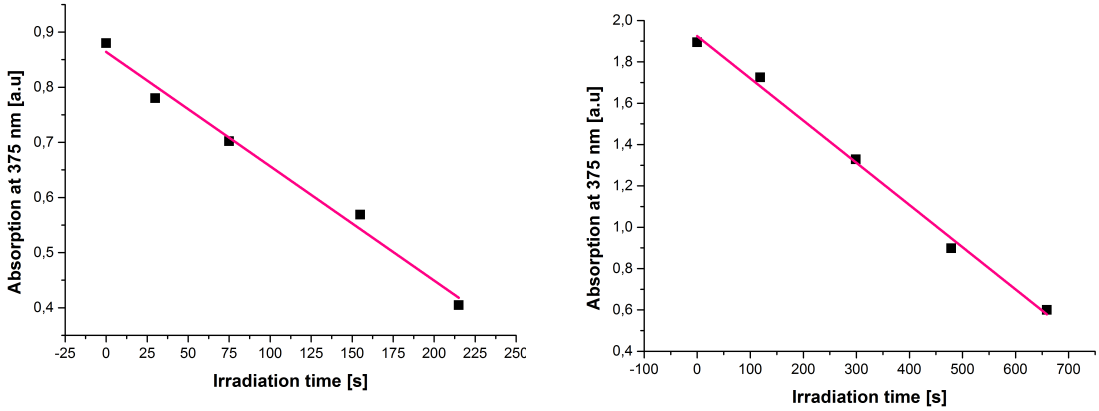


Figure S2.2. Absorption at 375 nm versus the irradiation time for the quantum yield measurements of the conversion of **4b** to **16b**. Experimental data is presented as squares and the line represents the linear fit.

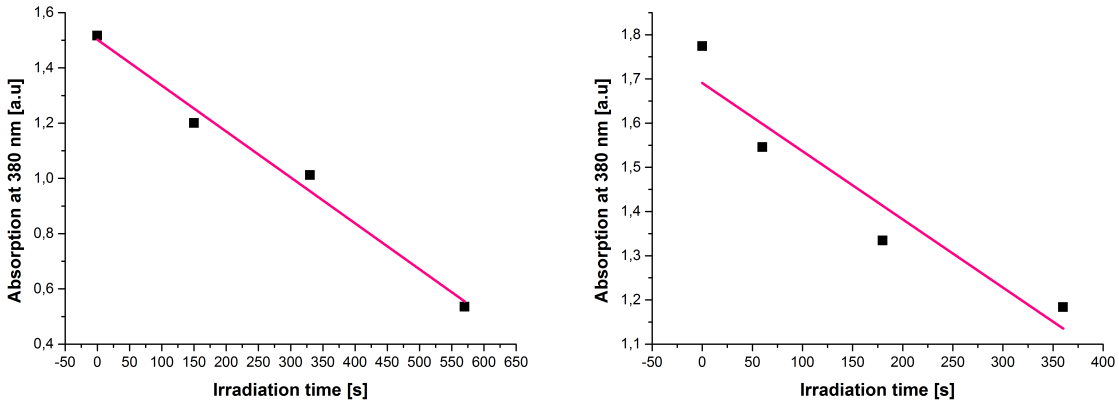


Figure S2.3. Absorption at 380 nm versus the irradiation time for the quantum yield measurements of the conversion of **4c** to**16c**. Experimental data is presented as squares and the line represents the linear fit.

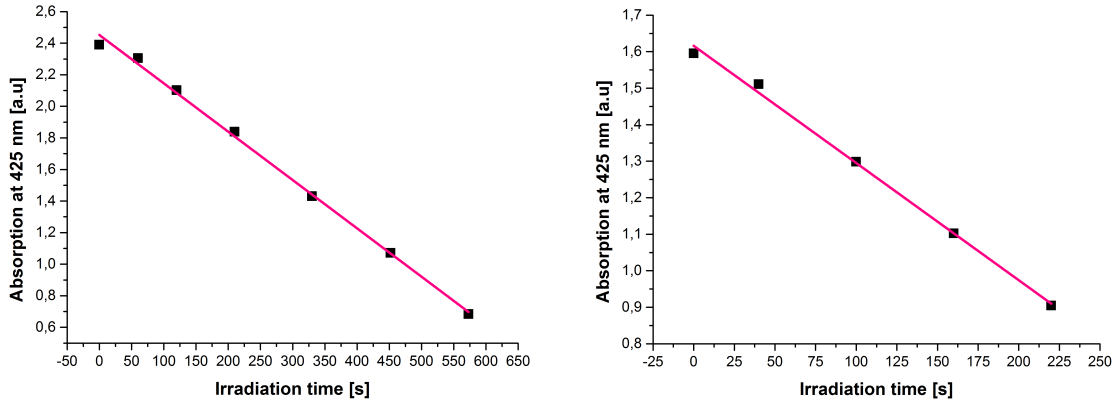


Figure S2.4. Absorption at 425 nm versus the irradiation time for the quantum yield measurements of the conversion of **4d** to **16d**. Experimental data is presented as squares and the line represents the linear fit.

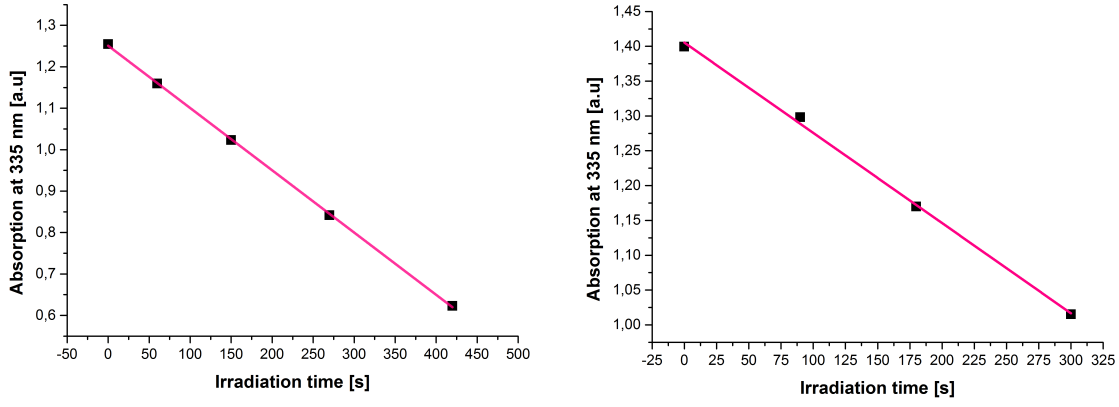


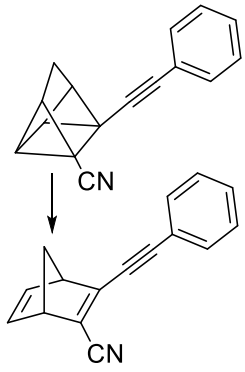
Figure S2.5. Absorption at 355 nm versus the irradiation time for the quantum yield measurements of the conversion of **5** to **17** Experimental data is presented as squares and the line represents the linear fit.

[1] C. A. Parker, *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1953**, *220*, 104-116; bC. G. Hatchard, C. A. Parker, *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1956**, *235*, 518-536.

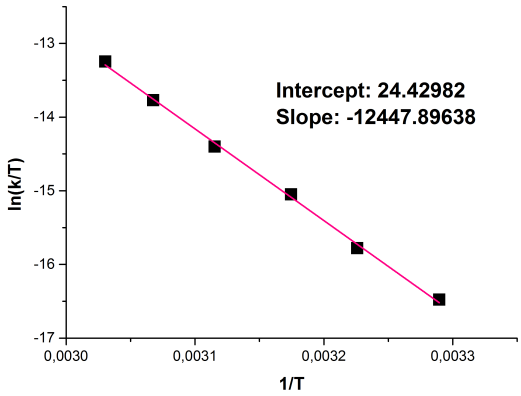
S.3 Kinetic Study of the Backconversion

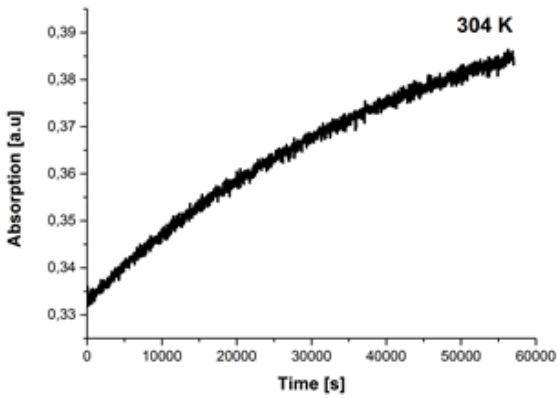
The norbornadienes were dissolved in toluene and irradiated with a metal-halide-UV lamp (366 nm) for 2-3 min, to obtain the corresponding quadricyclanes. Thereafter, the increase of the norbornadiene concentration over time were measured by recording the increase in absorption at 360 nm with a Cary 50 Bio UV/Vis-spectrophotometer for **16a - 16d** and a Cary 100 UV/Vis-spectrophotometer for **17**. The measurements were performed at six different temperatures 304 K, 310 K, 315 K, 321 K, 326 K, 330 K for the backconversion of **16a**-**16c**, 293 K, 298 K, 304 K, 315 K, 326 K for the backconversion of **16d** and 331 K, 336 K, 341 K, 346 K 351 K and 356 K for **17**.

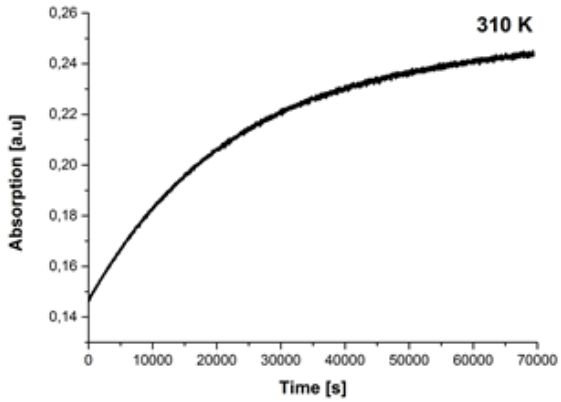
An exponential fit of the Eyring equation was applied to the obtained data to determine the rate constants at the different temperatures for all compounds. The enthalpy and entropy of activation was derived from the linear form of the Eyring equation.

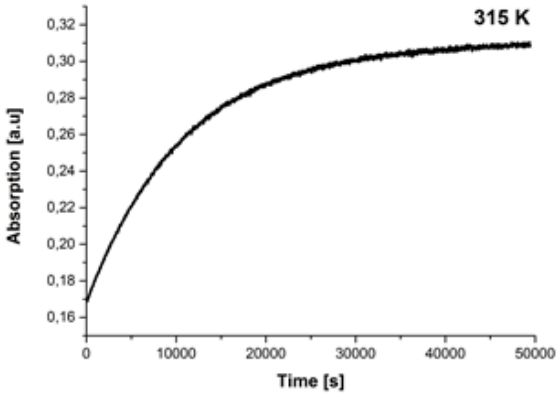


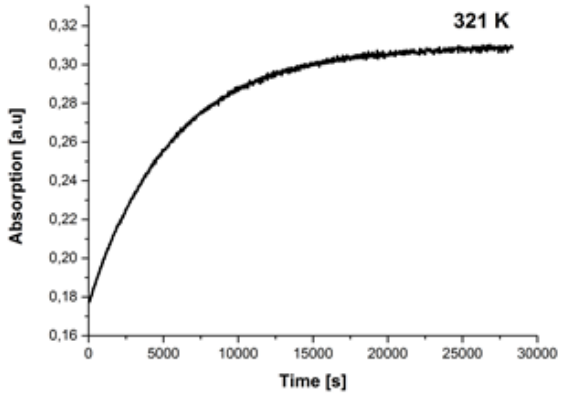
T [K]	k [s^{-1}]
304	2.1 x 10^{-5}
310	4.4 x 10^{-5}
315	9.2 x 10^{-5}
321	1.8 x 10^{-4}
326	3.4 x 10^{-4}
330	5.8 x 10^{-4}

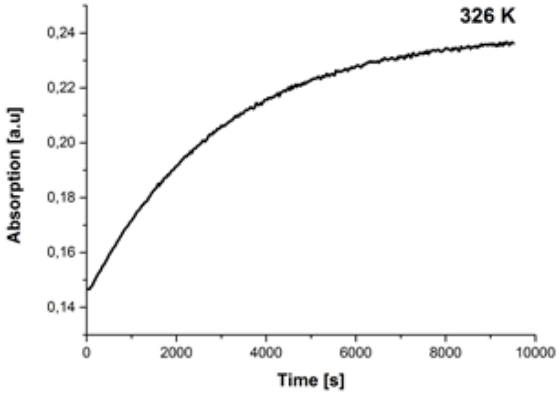












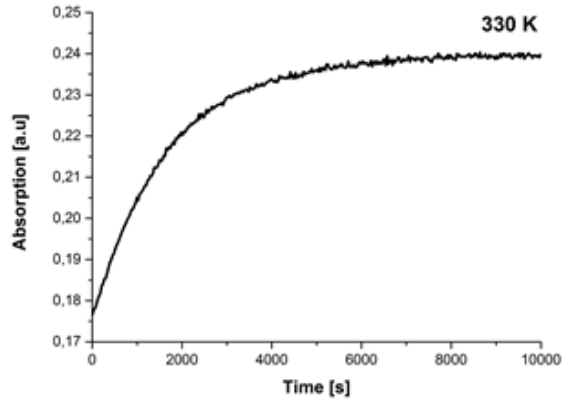
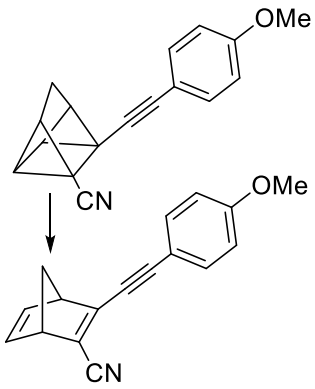
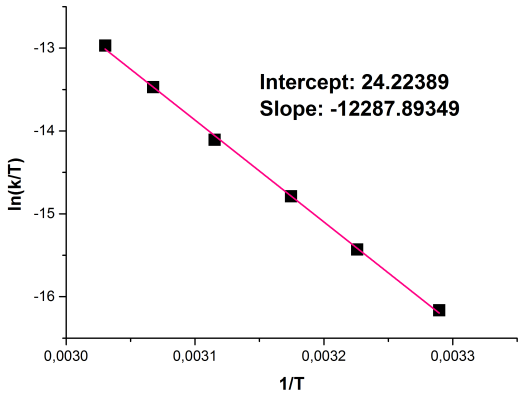


Figure S3.1. Kinetic study of the back conversion for **16a** to **4a**, obtained values of *k* and linear Eyring plot.



T [K]	k [s^{-1}]
304	2.9×10^{-5}
310	6.2×10^{-5}
315	1.2×10^{-5}
321	2.4×10^{-4}
326	4.6×10^{-4}
330	7.7×10^{-4}



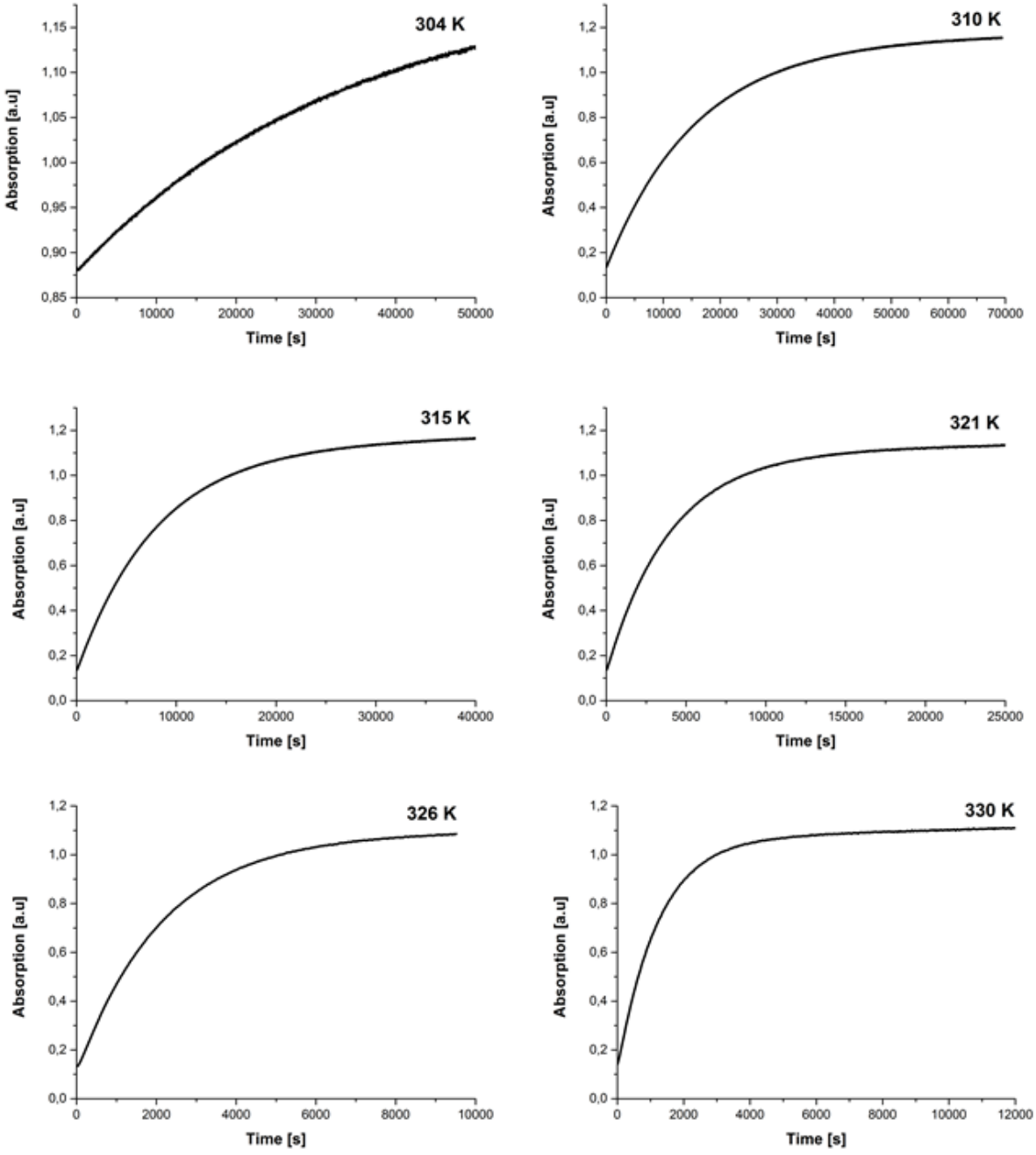
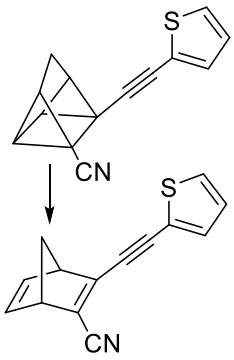
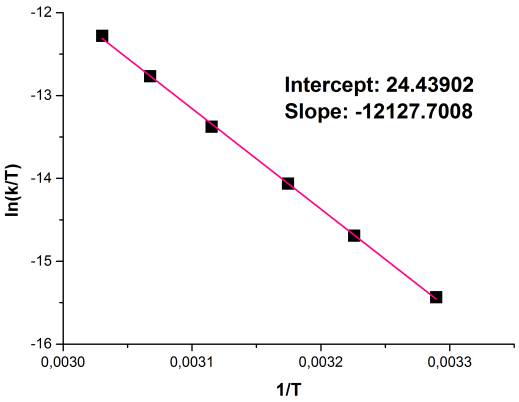
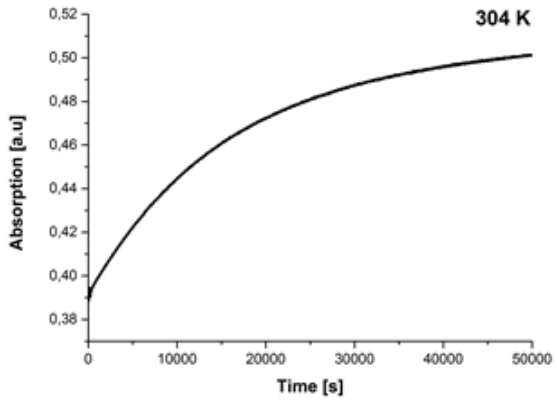


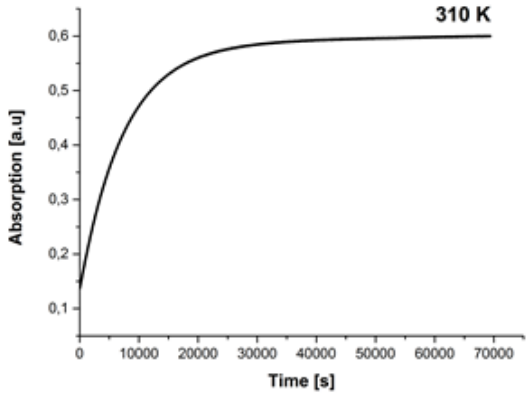
Figure S3.2. Kinetic study of the back conversion for **16b** to **4b**, obtained values of *k* and linear Eyring plot.

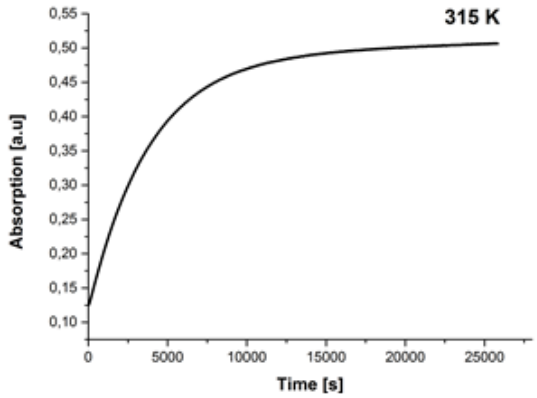


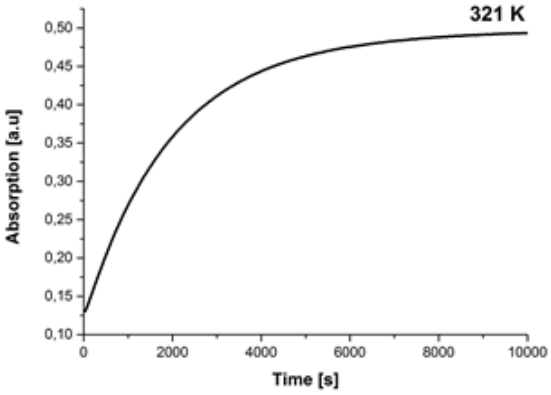
T [K]	k [s^{-1}]
304	6.0×10^{-5}
310	1.3×10^{-4}
315	2.5×10^{-4}
321	5.0×10^{-4}
326	9.3×10^{-4}
330	1.5×10^{-3}

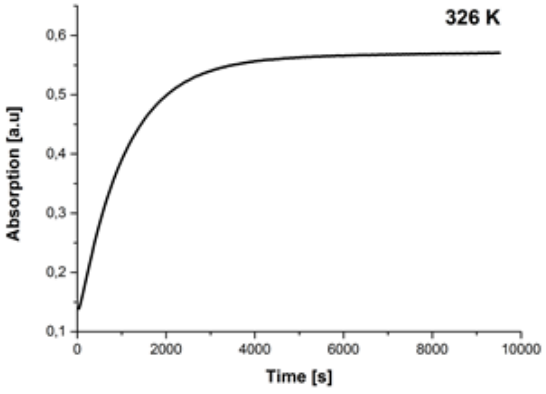












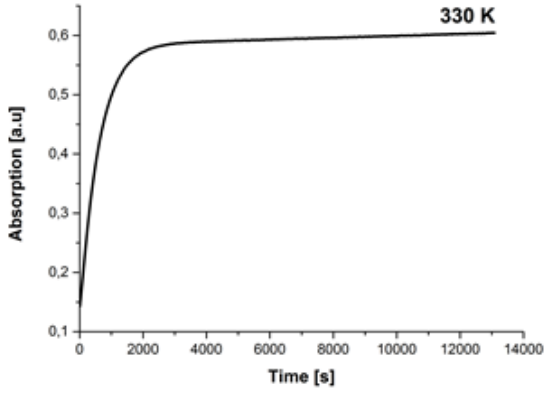
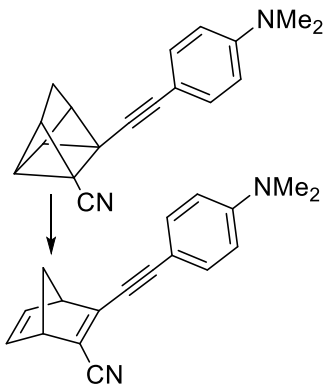
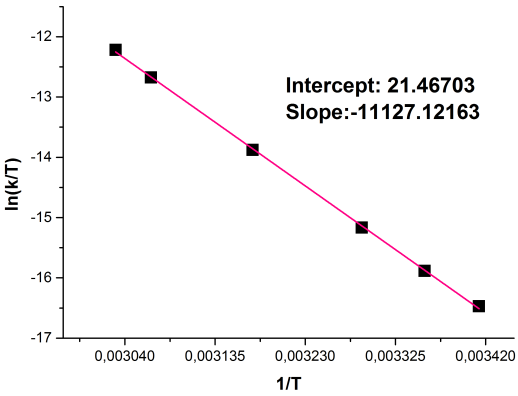


Figure S3.3. Kinetic study of the back conversion for **16c** to **4b**, obtained values of *k* and linear Eyring plot.



T [K]	k [s^{-1}]
293	2.1×10^{-5}
298	3.8×10^{-5}
304	7.9×10^{-5}
315	3.0×10^{-4}
326	1.0×10^{-3}
330	1.6×10^{-3}



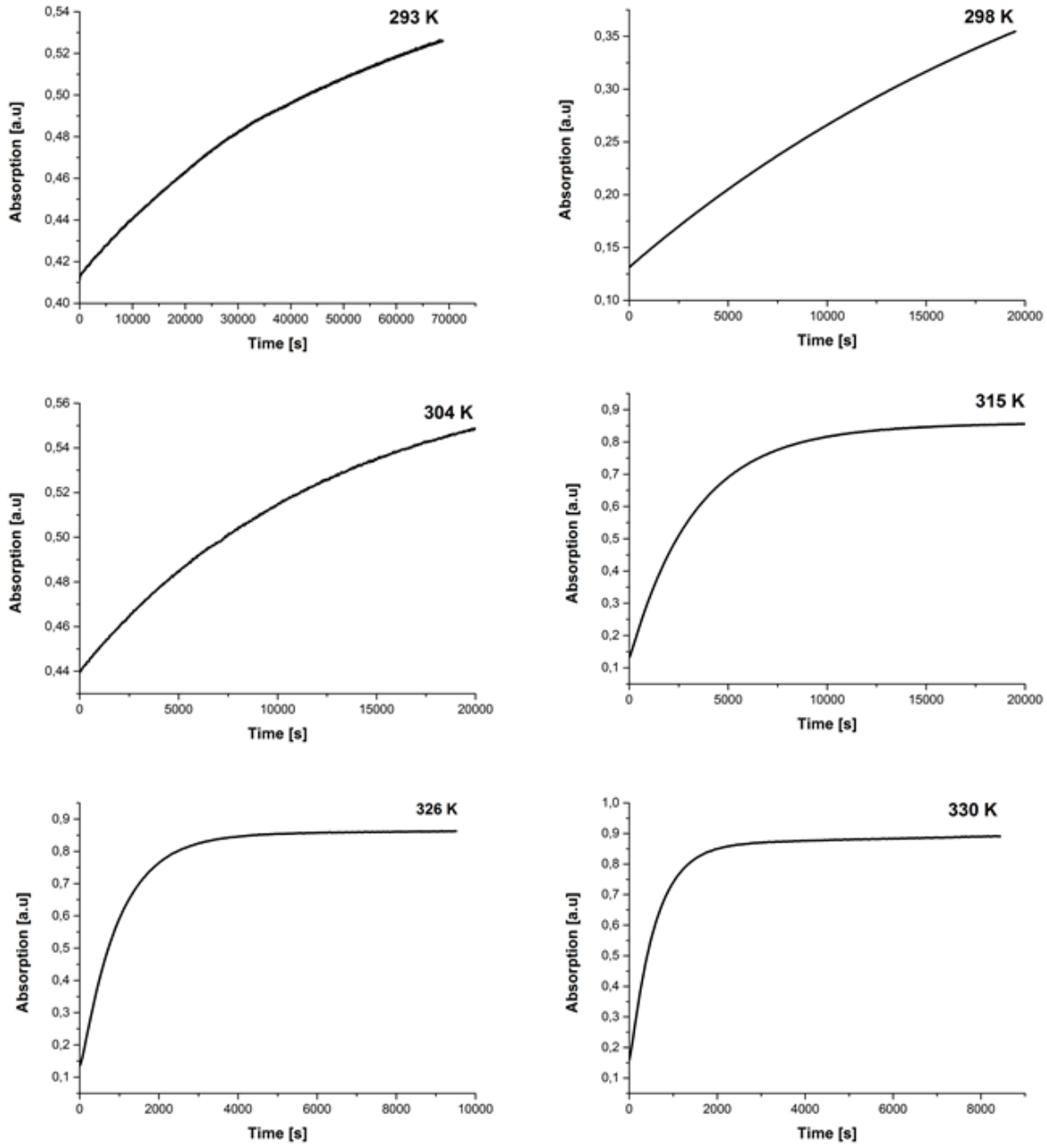
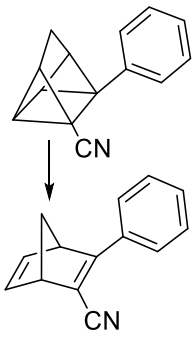
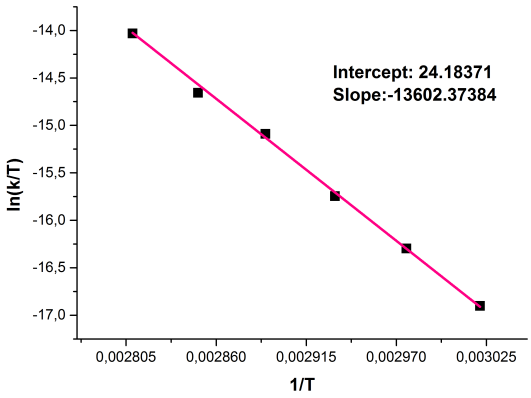


Figure S3.4. Kinetic study of the back conversion for **16d** to **4d**, obtained values of *k* and linear Eyring plot.



T [K]	k [s^{-1}]
331	1.5×10^{-5}
336	2.8×10^{-5}
341	4.9×10^{-5}
346	9.7×10^{-5}
351	1.5×10^{-4}
356	2.9×10^{-4}



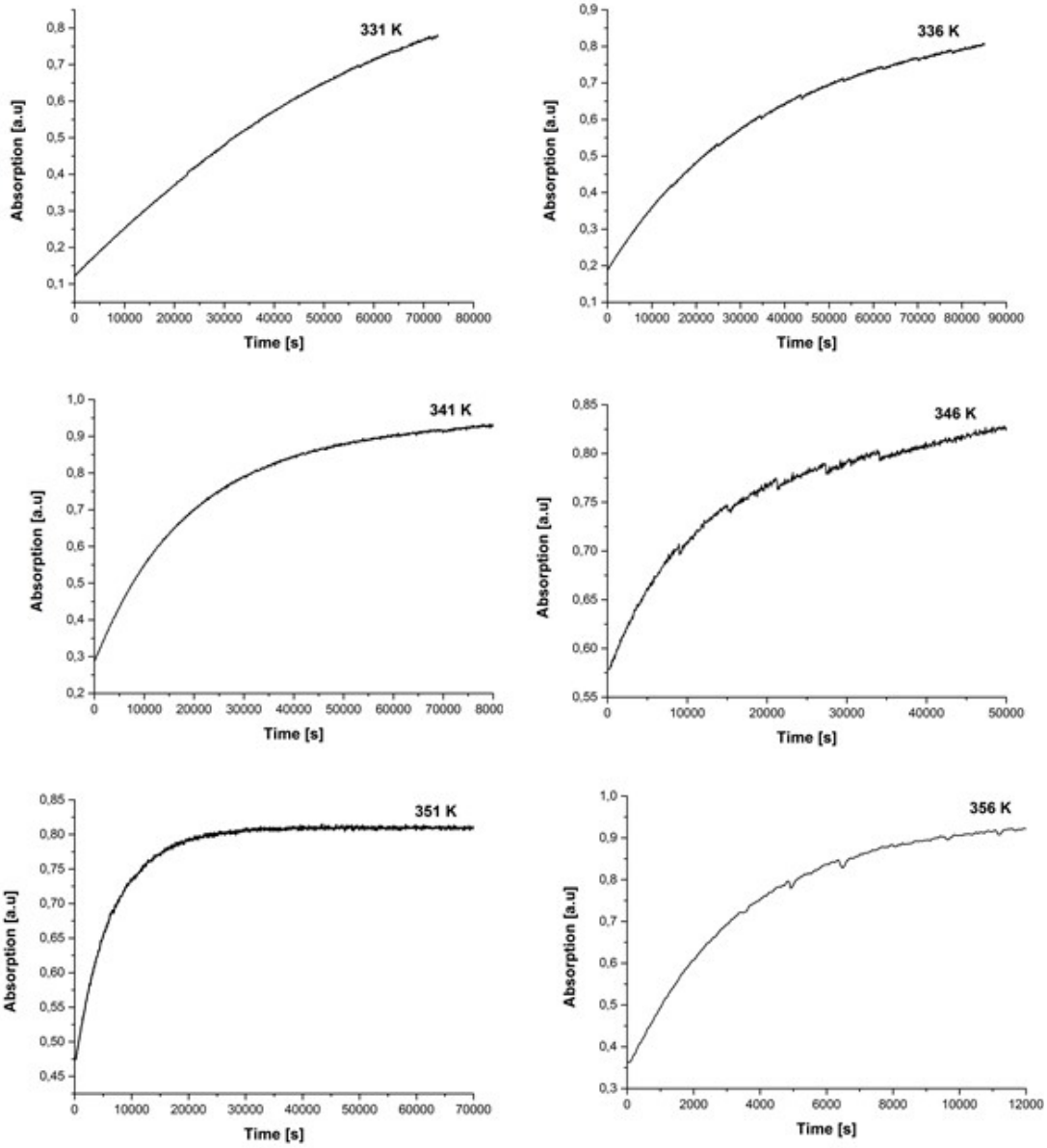


Figure S3.5. Kinetic study of the back conversion for **17** to **5**, obtained values of *k* and linear Eyring plot.

S.4 Differential scanning calorimetry (DSC)

The norbornadienes **4a**, **4b** , **4c**, **4d**, and **5** (about 15 mg) were dissolved in dichloromethane or tetrahydrofurane (about 3 mL). The solution was irradiated for 45 minutes to 6 hours using a fiber-coupled LED emitting at 365 nm or 310 nm. The solvent was evaporated, and about 1 mg of quadricyclane **16a**, **16b**, **16c**, **16d** and **17** were sealed in a 40 µl aluminium pan and inserted in the DSC at 0°C. The DSC method involved a double cycle of heating (at 10 °C/min from 0 to 180°C) and cooling (at 40 °C/min from 180 to 0°C), the thermograms from the first part of the experiment are presentes in Figure S4.1.

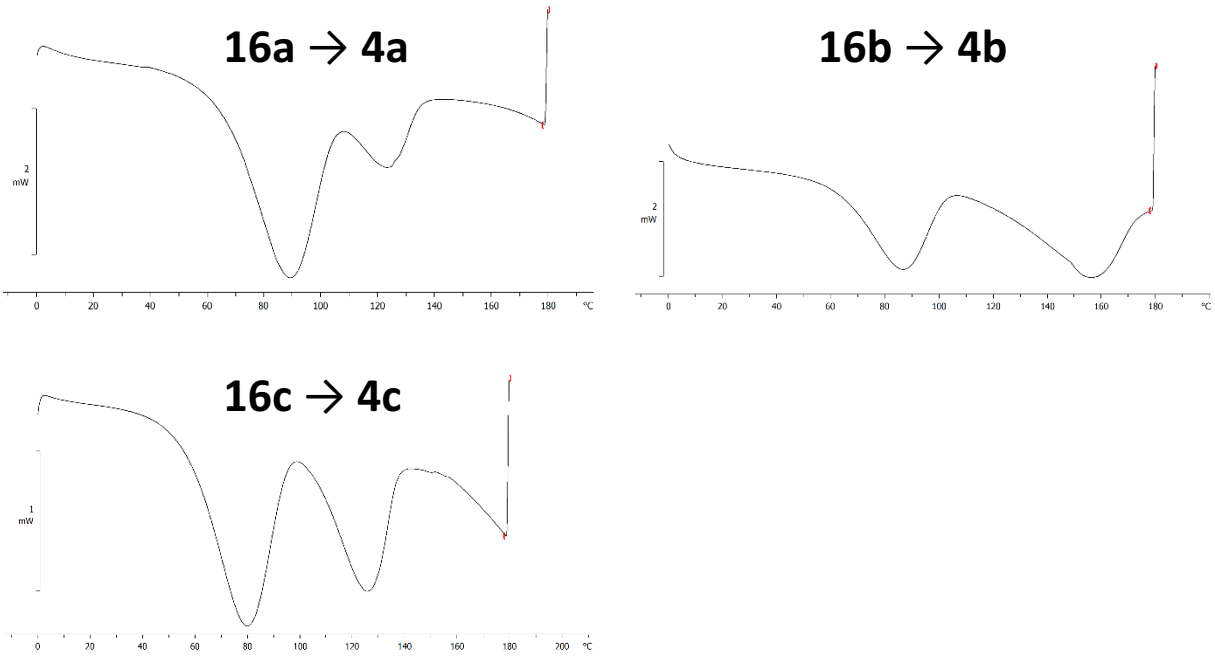


Figure S4.1. DSC thermograms showing the heat release peaks associated with thermal back conversion of quadricyclanes **16a**, **16b**, and **16c** to the corresponding norbornadienes.

In parallel with the DSC meaurments, the prepared quadricyclanes were also analyzed with ^{1}H-NMR spectroscopy to determine the amount of quadricyclane compared to norbornadiene. The amount of quadricyclane was corrected according to its relative amount with respect to the norbornadiene. Therafter, the measured energy release was normalized and the enthalpy of the isomerization was calculated (103 kJ/mol for **16d** to **4d** and 122 kJ/mol for **17** to **5**). For **16a**, **16b** and **16c** no values were calculated since more than one exothermic peak were obtained and it is not possible to distinguish eventual concurring phase changes processes from the thermal back isomerization.

S.5 xyz coordinates from calculations

Following is xyz coordinates for all compounds modelled in this study. For molecules (4b, 4c, 16b and 16c) where two rotational isomers has been identified, the structures are indexed as (i), (ii). The number first line denotes number of atoms in the molecule, the number in the second line denotes the total energy of the molecule in Hartree energies.

4a

28

-671.098091884

C -5.36838753 0.03915185 1.26987221

C -4.36170023 -1.02235305 1.80077599

C -5.88609669 0.35840038 2.70256754

H -6.13606812 -0.39003015 0.62341851

H -4.8889749 0.89077812 0.78191451

C -4.52485226 0.70670965 3.35293872

C -3.596742 -0.12879052 2.8143194

C -6.23971366 -1.06963923 3.15611259

H -6.65902271 1.11547799 2.81714933

C -5.33283308 -1.88879432 2.62142506

H -3.72718758 -1.54083361 1.08500557

H -5.22451434 -2.9553539 2.76991354

H -7.04145309 -1.31446598 3.84076246

N -4.23069792 2.47453228 5.18977981

C -4.34377884 1.66966507 4.36337329

C -2.2350129 -0.24882163 3.10142291

C 2.28880077 0.23284526 4.86292999

H 2.73809348 0.88233478 5.60689714

C 0.93302656 0.34715941 4.580205

C 3.06999662 -0.71127656 4.19533775

C 0.33598784 -0.48901557 3.61698964

C 2.4880541 -1.54483086 3.23936777

C 1.13318822 -1.43825781 2.94932297

H 3.09282814 -2.28000056 2.71862275

H 0.67851572 -2.08461466 2.2068481

H 0.32240944 1.07897494 5.09678742

C -1.04877116 -0.37169979 3.32768047

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4b (i)

32

-785.654082485

C -5.45310055 -0.08515326 1.26367279

C -4.36364442 -1.03753824 1.83643548

C -5.9843043 0.26548526 2.68368934

H -6.18892464 -0.60479871 0.64701574

H -5.04429245 0.77515956 0.72892245

C -4.65005342 0.75113036 3.3014832

C -3.66273327 -0.03776453 2.79631834

C -6.22343627 -1.16052778 3.21186119

H -6.81324643 0.96529936 2.76762774

C -5.25904092 -1.93348222 2.70962338

H -3.69569429 -1.5413037 1.14076202

H -5.06658663 -2.9792654 2.91149559

H -6.99858118 -1.43171957 3.91703481

N -4.47941451 2.62566409 5.04546495

C -4.53725372 1.77392608 4.26091264

C -2.29531458 -0.04046417 3.07443726

H 4.57293208 0.70499963 6.29817589

C 2.18176538 0.89796542 4.78549453

H 2.55778149 1.62769555 5.49105641

C 4.97839181 0.82593117 5.28882152

C 0.82211751 0.87781751 4.49442407

O 4.3791147 -0.08733484 4.37815703

C 3.03879477 -0.01945354 4.1664949

H 6.0391871 0.58394392 5.29481385

C 0.28536418 -0.04942542 3.58577718

C 2.51733978 -0.95186638 3.25682546

C 1.16553172 -0.96649609 2.97163489

H 3.19657948 -1.65457846 2.78752593

H 4.84430703 1.86123747 4.96015162

H 0.77090528 -1.69038846 2.26738735

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C -1.10153696 -0.05811073 3.29881183

4b (ii)

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C -6.22143287 -1.12614127 3.13380953

H -6.75384932 1.00801588 2.65806049

C -5.2508973 -1.91814739 2.67498688

H -3.61676128 -1.56055141 1.17140935

H -5.08559145 -2.96624993 2.88867254

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N -4.49203066 2.63524737 5.02662486

C -4.52953184 1.78179465 4.24277627

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4c (i)

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C -4.41676436 -0.91081164 1.74028771

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H -4.98264118 1.07722283 0.90159437

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H -6.80462303 1.04530877 2.90243617

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H -3.74953327 -1.33618004 0.9934982

H -5.2355341 -2.95505119 2.49473495

H -7.12870452 -1.48393566 3.67452605

N -4.48662892 2.2397552 5.4581342

C -4.54855897 1.51614511 4.55460339

C -2.34750702 -0.20887508 3.15905068

C 2.44818106 -1.09500168 3.62042311

C 1.1548194 -1.23228132 3.05981343

C 0.20377045 -0.44313262 3.67984133

S 0.93403459 0.48464625 4.98290623

C -1.15943558 -0.32897468 3.38874435

C 2.4826389 -0.20553276 4.66238298

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4c (ii)

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C -1.14194128 -0.30696139 3.28050005

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H -5.02576254 -2.92924771 3.10965949

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C 3.24815827 -0.34179897 4.19910448

H 6.44672345 -1.31929848 4.27496375

C 0.45726623 -0.25138962 3.6149451

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C 1.28902199 -1.2439889 3.06159944

H 3.23318835 -2.08144118 2.89437776

H 5.08621556 -2.44597462 4.36385306

H 0.85688628 -1.98816027 2.40112394

H 0.44010192 1.4649296 4.91902489

C -0.92549628 -0.20019825 3.32957486

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26

-594.921311406

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C 3.50947632 0.02419737 -3.35705833

C 5.89006769 -0.04649048 -3.76946388

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C 5.01413347 -0.72379073 -1.62466933

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H 2.50941948 0.22992271 -3.71825537

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16a

28

-671.051924721

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H -6.92092497 -0.84511122 3.76408533

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C 1.21750549 -3.71704258 4.97593588

H 1.74291743 -3.44741499 5.88642071

C 0.04227456 -3.05367521 4.64079723

C 1.72000223 -4.723324 4.15068597

C -0.65189446 -3.38861975 3.46375833

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H 1.42356561 -5.84495887 2.33546899

H -0.66507733 -4.66717407 1.72787431

H -0.34916929 -2.27230926 5.28256479

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H 2.6369613 -5.23912352 4.41636163

16b (i)

32

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H -5.60818271 1.58253763 1.30816066

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H -6.78378029 0.44752877 3.45642367

C -4.89536378 -1.32255811 1.19178637

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H -7.02040923 -1.8269871 2.07938662

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H 2.75671087 -3.47970352 2.18100671

C 3.22955049 -5.97336015 5.20569152

C 0.68989058 -2.94678407 2.46478008

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C 1.91079599 -4.47882279 3.87881885

H 4.25679451 -6.33250795 5.18765137

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C -0.40987671 -3.99333575 4.33781174

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H 3.042361 -5.45953663 6.15420478

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16b (ii)

32

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H -4.9680496 1.60979493 2.80187156

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C 2.12109013 -2.72833987 1.5343696

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O 3.84913829 -3.70508523 2.96230829

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C -1.43245309 -1.93241659 2.39592684

16c (i)

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C -4.07261279 -1.31314663 2.49697796

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H -6.49981567 1.09242487 3.05169559

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H -3.69428526 -0.87382145 0.32720554

H -5.38258321 -2.76163819 1.18602321

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C 1.01062059 -4.87551674 4.3306219

H 2.65752678 -3.54808459 3.88299853

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16c (ii)

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H 4.51985023 -3.9111371 4.53151023

H 4.37142724 -5.04684779 3.17488114

17

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C 5.80972652 -0.0599315 -3.71879614

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H 7.18913299 -0.17943021 -2.06893633

H 5.42639038 -0.45336743 -0.36791355

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H 3.64084278 -0.52531894 1.4056695

H 1.16523629 0.85808426 1.51902348

Solar Conversion

A stirred solution of **4d** (Toluene, 3.1×10^{-5} M) in a quartz cuvette was exposed to simulated (EYE Solarlux solar simulator (class B/C)) 1.5 AM solar spectrum for stepwise irradiations of about 1s. After each irradiation the conversion was monitored with UV-Vis spectroscopy. The recorded spectra are shown in Figure SI1:

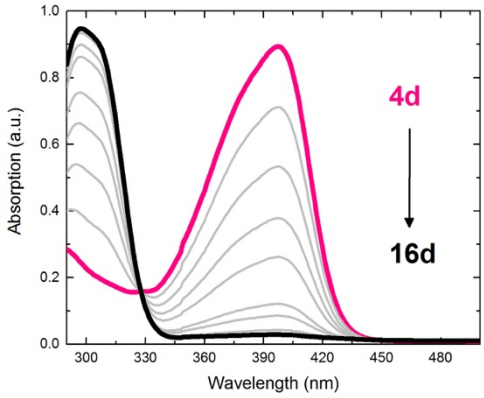

Figure SI1 Sunlight induced stepwise photoconversion of **4d** (toluene, 3.1×10^{-5} M).