Supporting Information

Generation and Interception of Bicyclo[3.2.1]oct-2-yne: An Experimental and Theoretical Mechanistic Study

T. E. Anderson,[a] Beauty K. Chabuka,[b] Igor V. Alabugin,*[b] Dasan M. Thamattoor,*[a] and David Lee Phillips*[c]

[a] Department of Chemistry, Colby College, Waterville, ME 04901 United States

[b]Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306 United States

[c]Department of Chemistry, The University of Hong Kong, The University of Hong Kong, Pok Fu Lam 999077, Hong Kong, S.A.R., P. R. China

*[a]E-mail: dmthamat@colby.edu

*[b]E-mail: alabugin@chem.fsu.edu

*[c]E-mail: phillips8hk@gmail.com

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General Notes.

Tetrahydrofuran was degassed by purging with nitrogen, and dried by passage through two activated alumina columns (2 ft × 4 in). Other solvents and reagents were used as obtained from commercial sources. Medium pressure flash chromatography was performed on an automated system using prepacked silica gel columns (70−230 mesh), or by hand using Sorbtech silica gel 60A (35 x 70 mesh) with the indicated eluents. $AgNO_3$-treated silica gel was prepared as follows: To a solution of $AgNO_3$ (12.0 g) in acetonitrile (100 mL) was added silica gel (40 g). The mixture was stirred, and the resulting slurry was heated at 80 °C *in vacuo* on a rotary evaporator for 2 h, then allowed to cool to room temperature and stored in a foil-covered flask. Proton (^{1}H) and proton-decoupled carbon $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ at 500 and 126 MHz, respectively. The data are reported as follows: chemical shift in ppm referenced to residual solvent (^{1}H NMR: $CDCl_3$ δ 7.26; ^{13}C NMR: $CDCl_3$ δ 77.2, multiplicity, coupling constants (Hz), and integration. Structures were determined using COSY, HSQC, and HMBC experiments. Overlapping carbon peaks were identified using HSQC experiments and integration of ^{13}C NMR spectra. High resolution mass spectra (HRMS) data were obtained on an Agilent 6230 TOF Mass Spectrometer. Infrared spectra (resolution 4.0 cm^{-1}) were acquired on solid samples with an FTIR instrument equipped with an attenuated total reflectance (ATR) accessory. Photolysis experiments were conducted with a Newport 200 W Xe-Hg arc lamp (model # 6290; horizontal intensity 600 cd) with a Newport 280–400 dichroic mirror (model # 66245) fitted in a Newport 67005 Housing with a Newport 69907 Universal Arc Lamp Power Supply. All photolysis reactions were conducted in quartz glassware positioned 30 cm away from the light source. All reactions were performed under an atmosphere of argon in glassware that had been dried in an oven at 120 °C unless otherwise stated.

Computational Procedures.

All quantum chemical calculations, except NBO, were performed using Orca (version 5.0).[1-3] Geometries were optimized using hybrid density functional theory (M06-2X)[4] using Ahrlich's def2-TZVP basis set.[5] Frequency calculations were performed to verify the nature of the stationary points as minima (0 imaginary frequency) or maxima (1 imaginary frequency). Single point energy calculations were performed using domain-based local pair natural orbital coupled-cluster [DLPNO-CCSD(T)][6-15] methods in combination with Ahrlich's def2-TZVPP basis set.[5] The auxiliary basis sets def2/J[16] and def2-TZVPP/C[17-18] were also used for density functional theory and coupled-cluster methods, respectively. All density functional theory calculations used Grimme's atom-pairwise dispersion correction with Becke–Johnson damping (D3BJ).[19-21] Acceleration of SCF and exchange integral calculations was accomplished by invoking the resolution-of-identity[22] option and the chain-of-spheres[23-25] algorithm, respectively (RIJCOSX). Solvent effects were incorporated using the conductor-like polarizable continuum model (CPCM).[26] T1 diagnostic values[27] for coupled-cluster calculations were <0.02, indicating that the systems are adequately described by a single reference wave function. Transition state geometries were calculated using nudged elastic band with transition state optimization (NEB-TS)[28-30].

GaussView (version 6.0)[31] and/or ChemCraft[32] were used to visualize computational data. Gibbs free energies were determined from the computational data by adding the electronic energy E_{el}, calculated at the DLPNO-CCSD(T) level, to the Gibbs free energy minus the electronic energy (G-E_{el}), calculated at the M06-2X level.[33] NBO calculations[34] were performed with Gaussian 16[35] at M06-2X/D3/6-311++G(d,p) level of theory in gas phase.

Supplementary Figures.

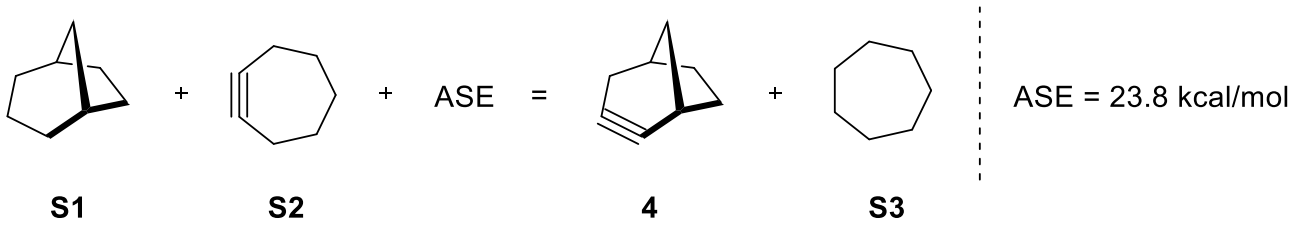


Figure S1. Alkynyl strain energies (ASE) in bicyclo[3.2.1]oct-2-yne (**4**) relative to monocyclic cycloheptyne (**S2**). Based on isodesmic equations similar to those described by Bach,[36] calculated at the DLPNO-CCSD(T)/def2-TZVPP//M06-2X/def2-TZVP level of theory.

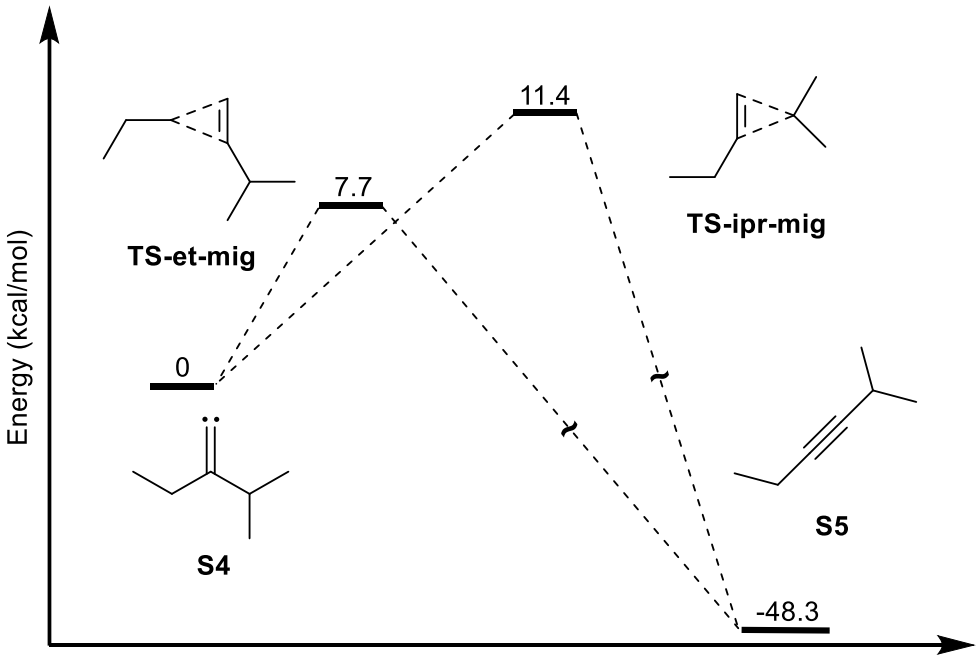


Figure S2. Potential energy surface for the FBW rearrangement of ethyl isopropyl alkylidene carbene (**S4**) to 2-methylhex-3-yne (**S5**), involving migration of the ethyl group (via **TS-et-mig**) or the isopropyl group (via **TS-ipr-mig**), computed at CCSD(T)/def2-TZVPP//M06-2X/def2-TZVP

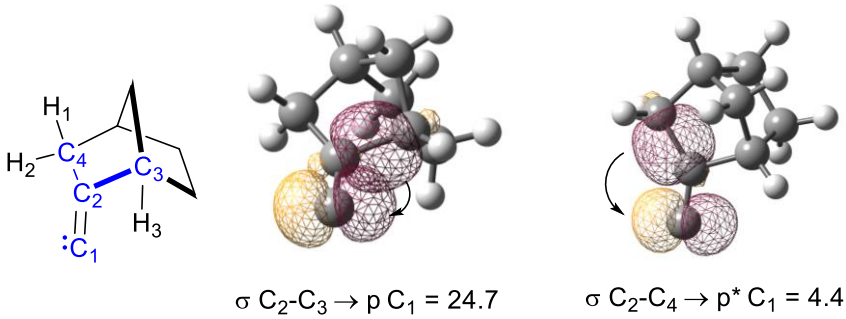


Figure S3. NBO analysis showing hyperconjugative interactions of vacant p orbital on C_1 with the C_2-C_3 and C_2-C_4 bonds in the carbene. [Beauty/Igor: Please add a structure for the C_2-C_4 bond with the p orbital.]

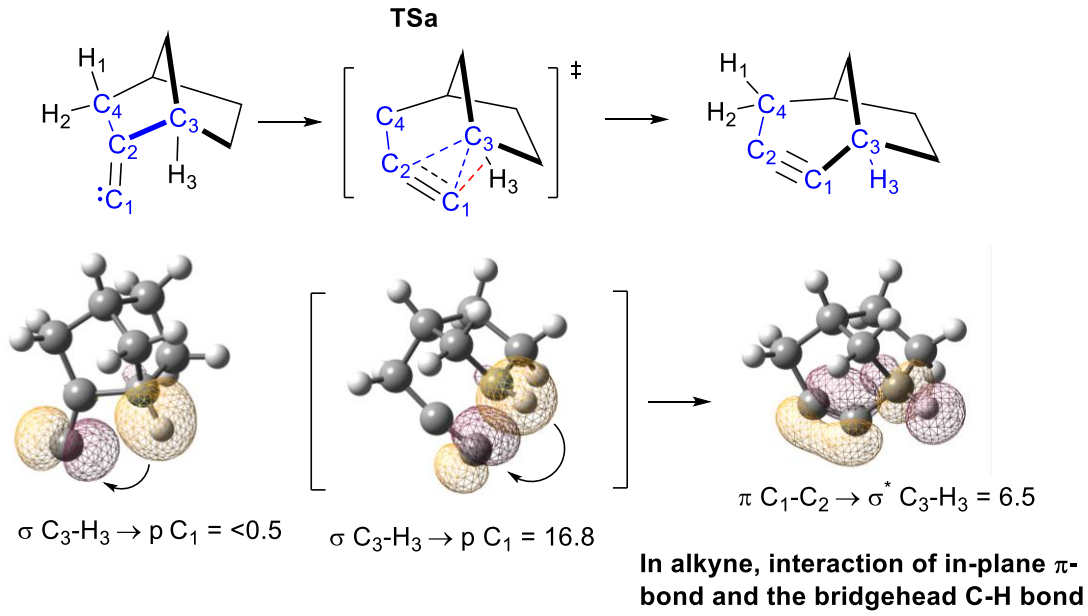
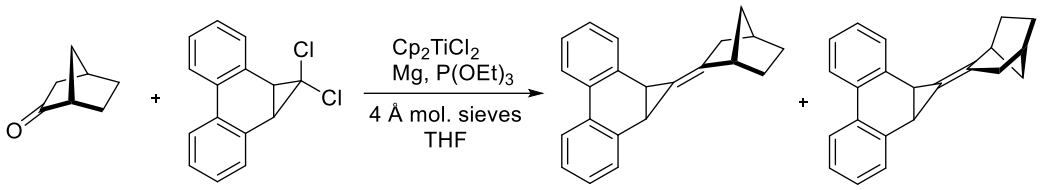


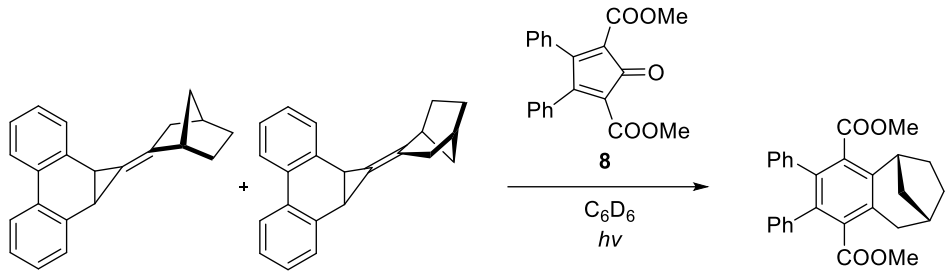
Figure S4. NBO analysis showing the weak interaction between C_3-H_3 bond and the vacant p orbital on C_1 in the carbene which then gains substantial importance in TSa and remains significant in the product alkyne.

Synthetic Procedures.



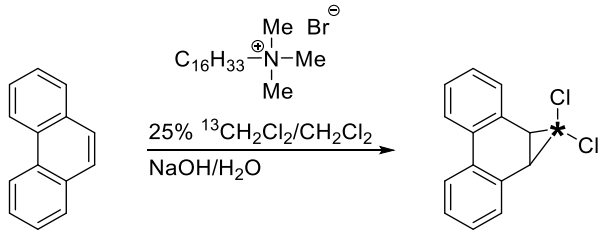
5 **6** **7**

Precursor 7: Following the procedure of Takeda *et al.*,[37] to a round-bottom flask charged with magnesium turnings (0.365 g, 15.0 mmol) and 4 Å molecular sieves (0.750 g) was added bis(cyclopentadienyl)titanium(IV) dichloride (3.73 g, 15.0 mmol) followed by anhydrous THF (30 mL). Triethyl phosphite (5.14 mL, 30.0 mmol) was added and the reaction mixture was stirred for 3 h, during which the color of the mixture turned from red to dark green. A solution of dichlorocyclopropyl phenanthrene **6** (1.31 g, 5.00 mmol) dissolved in THF (10 mL) was added and the reaction mixture was stirred for an additional 30 min. Norcamphor (**5**, 0.275 g, 2.50 mmol) in THF (5 mL) was then added, and the reaction mixture was stirred for an additional 16 h. Hexanes (100 mL) was added, and the resulting suspension was transferred to a plug of silica and eluted with hexanes (100 mL) followed by a solution of hexanes and ethyl acetate (10:90, 40 mL). The elution was concentrated *in vacuo* to yield precursor **7** as a mixture of diastereomers in a 1.0:1.0 ratio. Purification of the resulting residue by flash chromatography with silica gel (hexanes) followed by flash column chromatography with $AgNO_3$-treated silica gel (30% $AgNO_3$, 2:98→20:80 ethyl acetate:hexanes) afforded precursor **7** as a mixture of diastereomers in 1.0:0.45 ratio as a white solid (0.190 g, 33%): mp = 96–104 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2.9H), 7.44–7.31 (m, 2.9H), 7.26–7.19 (m, 5.8H), 3.16–3.08 (m, 2.45H), 3.07–3.02 (m, 0.45H), 2.78 (d, *J* = 3.1 Hz, 1H), 2.68 (d, *J* = 2.9 Hz, 0.45H), 2.30–2.23 (m, 1.45H), 2.21–2.14 (m, 1H), 1.99–1.86 (m, 0.9H), 1.69–1.56 (m, 1.9H), 1.44–1.21 (m, 4.9H), 1.15–1.10 (m, 0.45H), 1.07–1.02 (m, 0.45H), 0.87–0.79 (m, 1H), 0.47–0.38 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6 (major), 135.4 (minor), 134.8 (major), 134.7 (minor), 134.3 (major), 134.0 (minor), 129.4 (major), 129.34 (minor), 129.31 (minor), 129.26 (major), 128.94 (minor), 128.86 (major), 128.85 (minor), 128.6 (major), 127.8 (major), 127.7 (minor), 127.61 (minor), 127.57 (major), 125.83 (minor), 125.77 (2C, major, minor), 125.7 (major), 123.41 (major), 123.35 (minor), 123.33 (minor), 123.2 (major), 113.3 (major), 112.3 (minor), 43.8 (major), 43.1 (minor), 39.4 (major), 39.3 (minor), 37.0 (major), 36.8 (minor), 36.5 (2C, major, minor), 29.4 (minor), 28.8 (major), 28.6 (minor), 28.0 (major), 22.5 (major), 22.2 (major), 22.12 (minor), 22.05 (minor). IR (ATR) 3060, 3025, 2956, 2864, 1599, 1485, 1438 cm^{-1}. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}$ 285.1638; Found 285.1659.



7 **10**

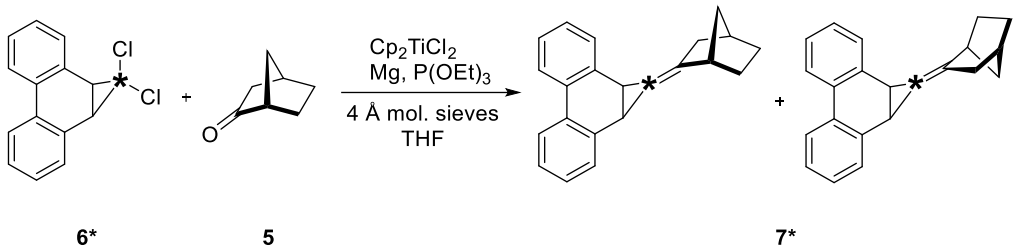
Photolysis of 7: Precursor **7** (0.110 g, 0.385 mmol) and 2-oxo-4,5-diphenyl-cyclopenta-3,5-diene-1,3-dicarboxylic acid dimethylester (**8**, 0.134 g, 0.385 mmol) were dissolved in deuterated benzene (5 mL) and transferred to an argon-flushed quartz cuvette. The reaction mixture was placed in front of a mercury lamp and irradiated until the starting material was consumed, as determined by ^{1}H NMR analysis of the reaction mixture (22 h). The benzene was then removed *in vacuo*, and purification of the resulting residue by flash chromatography (2:98→10:90 ethyl acetate:hexanes) afforded adduct **10** as a white solid (0.062 g, 38%): mp = 159–162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18–6.99 (m, 8H), 6.97–6.87 (m, 2H), 3.51–3.41 (m, 6H), 3.20–3.06 (m, 2H), 2.65–2.54 (m, 2H), 2.06–1.90 (m, 3H), 1.87–1.80 (m, 1H), 1.80–1.73 (m, 1H), 1.65–1.51 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7 (C), 169.6 (C), 141.3 (C), 138.43 (C), 138.39 (C), 136.6 (C), 136.34 (C), 136.30 (C), 134.0 (C), 131.2 (C), 130.4 (CH), 130.2 (CH), 129.9 (CH), 127.5 (2C), 126.9, 51.9 (2C), 38.8, 37.4, 35.9, 35.1, 33.1, 29.9. IR (ATR) 2948, 1726, 1432, 1314, 1197, 761, 698 cm^{-1}. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{26}O_4$ 427.1904; Found 427.1906.



S1 **6***

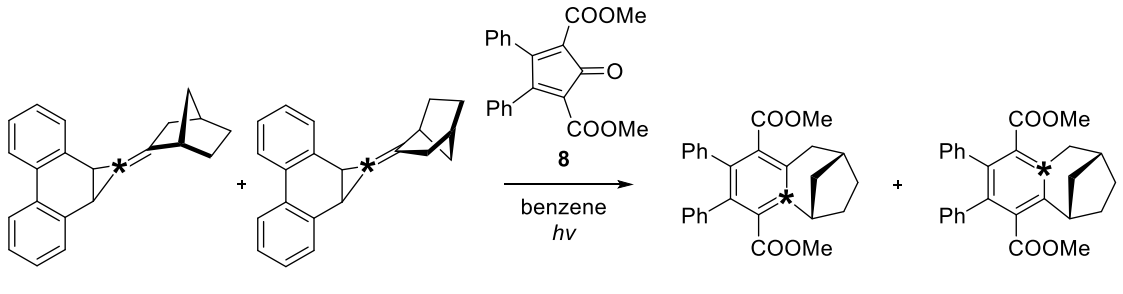
^{13}C-Labelled dichlorocyclopropyl phenanthrene 6*: To a pear-shaped round-bottom flask was added chloroform-^{13}C (7.50 mL, 83.8 mmol), chloroform (22.5 mL, 251 mmol), and phenanthrene (**S1**, 26.0 g, 146 mmol). The flask was cooled to 0 °C in an ice bath, and hexadecyltrimethyl ammonium chloride (0.467 g, 1.46 mmol) was added. Aqueous sodium hydroxide (55 mL, 50% *w/v*) was then added via addition funnel over 15 min. The addition funnel was replaced with a dry condenser, and the reaction mixture was heated at 50 °C in a heating mantle for 24 h. Water (350 mL) was then added to the reaction mixture, and the insoluble material was removed by filtration then purified by flash column chromatography (hexanes). The organic layer was separated from the filtrate and the solvent was removed *in vacuo*. The resulting solid was purified by recrystallization from hexanes. Purification yielded ^{13}C-labelled dichlorocyclopropyl phenanthrene (**6***) as a white, flakey solid (5.88 g, 15%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.43–7.37 (m, 2H), 7.37–7.31 (m, 2H), 3.41 (s, 1H).^{13}C

NMR (500 MHz, $CDCl_3$) δ 131.4, 131.1, 128.3, 128.2, 128.1, 123.2, 59.0 (C*), 36.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{10}Cl_2$ 260.0160; Found 260.0172.



6* **5** **7***

Precursor 7*: According to the procedure of Takeda *et al.*,[37] to a round-bottom flask charged with magnesium turnings (0.182 g, 7.50 mmol) and 4 Å molecular sieves (0.375 g) was added bis(cyclopentadienyl)titanium(IV) dichloride (1.87 g, 7.50 mmol) followed by anhydrous THF (14 mL). Triethyl phosphite (2.57 mL, 15.0 mmol) was added and the reaction mixture was stirred for 3 h, during which the color of the mixture turned from red to dark green. A solution of ^{13}C-labelled dichlorocyclopropyl phenanthrene (**6***) dissolved in THF (5 mL) was added and the reaction mixture was stirred for an additional 30 min. Norcamphor (**5**, 0.138 g, 1.25 mmol) in THF (5 mL) was then added, and the reaction mixture was stirred for an additional 16 h. Hexanes (50 mL) was added, and the resulting suspension was transferred to a plug of silica and eluted with hexanes (50 mL) followed by a solution of hexanes and ethyl acetate (10:90, 20 mL). The elution was concentrated *in vacuo*, and purification of the resulting residue by flash chromatography (0:100→10:90 ethyl acetate:hexanes), followed by recrystallization from hexanes, afforded precursor **7*** as a mixture of diastereomers in 1.0:1.0 ratio as a white solid (0.027 g, 8%): Spectroscopic data are in agreement with those reported for precursor **7**



7* **10a*** **10b***

Photolysis of 7*: Following the procedure for the photolysis of **7**, Precursor **7*** (0.027 g, 0.095 mmol) and 2-oxo-4,5-diphenyl-cyclopenta-3,5-diene-1,3-dicarboxylic acid dimethylester (**8**, 0.035 g, 0.10 mmol) in benzene (1.2 mL) were irradiated for 22 h. Purification of the resulting residue by flash chromatography (2:98→10:90 ethyl acetate:hexanes) afforded adduct **10*** as a white solid as a mixture of isotopomers **10a*** and **10b*** (0.002 g, 5%). Spectroscopic data are in agreement with those reported for compound **10**.

Computational Data.

Coordinates and energies for CCSD(T)/CPCM$_{(benzene)}$/def2-TZVPP//M06-2X/ CPCM$_{(benzene)}$/def2-TZVP optimized structures (at 298 K)

2-Norbornylidene carbene (3)

Charge = 0, Multiplicity = 1

C	0.13413749453814	0.03794565643607	-0.00310287457049
C	1.65851633644041	0.25163042879527	-0.00990445150073
C	0.82877358431929	2.36008567053229	-0.01242569458248
C	-0.43468746532210	1.48519252232522	-0.00165949355121
H	-0.19494836579759	-0.53902910106422	-0.86727131972641
H	-0.17283408496560	-0.50077269668539	0.89314479586524
H	-1.07934041235378	1.69538462905380	-0.85250768814032
H	-1.00121470582402	1.68288540817492	0.90954318905963
C	1.80696461237876	1.52524654469455	0.83309953606170
H	2.82004313625681	1.92666825165639	0.83998474636137
H	1.44653460586926	1.40783758150702	1.85654802374056
C	2.07087324357303	0.75133035880467	-1.40405223813808
H	3.15449414134055	0.80895195392197	-1.50947041300418
H	1.67286324691433	0.14171689161377	-2.21431855238473
H	2.23121866782614	-0.61199663839336	0.32128199771033
H	0.67774723031572	3.39545920736295	0.27663334537364
C	1.48838480916582	2.15761492608658	-1.40975917801630
C	1.42578040532482	3.20331063517747	-2.15101252055754

G–E(el) = 0.12721547 Hartree
Final single point energy E(CCSD(T)) = -310.155403410154 Hartree

Bicyclo[3.2.1]oct-2-yne (4)

Charge = 0, Multiplicity = 1

C	0.02139900153541	0.32061911735949	-0.40006903290744
C	1.57270890865824	0.34088081916771	-0.47899717784964
C	0.87665500856087	2.38176494434764	0.60800771504362
C	-0.40691937626371	1.54454867756673	0.45698949469599
H	-0.41525743042699	0.36319399321632	-1.39792760675913
H	-0.32336614769237	-0.60410051337133	0.06175349763927
H	-1.21624601474327	2.11039057596204	-0.00097774717048
H	-0.73663562055414	1.22622472709581	1.44788608806614
C	1.94095374625342	1.25378536356891	0.70674471325127
H	2.96534728791365	1.62409419158969	0.67103663752442

H	1.79167777283049	0.71126713275355	1.64432528539960
C	2.06002287613748	0.93181330027405	-1.84695253619123
H	3.14366811645408	0.87002772559713	-1.95733803083472
H	1.59878309274473	0.39780337879916	-2.67791740719970
H	1.99824846070236	-0.65727557829583	-0.36680332181005
H	0.86288568246086	3.06950817145120	1.44957996845057
C	1.19938632451030	2.96529886355357	-0.73727379336744
C	1.59999479091858	2.32961733936416	-1.68731552598102

G–E(el) = 0.12925857 Hartree
Final single point energy E(CCSD(T)) = -310.172033325805 Hartree

Transition state TSa

Charge = 0, Multiplicity = 1

C	-0.90407597751963	-1.07146203356069	0.17186479058101
C	0.62802624154767	-0.89113693466403	0.22063086747919
C	-0.25811435489861	1.26775466769126	0.26036521010527
C	-1.48751815836290	0.36890270018051	0.26309250170497
H	-1.21416811988181	-1.58450374690885	-0.73856611971717
H	-1.23885007985791	-1.67300328422090	1.01628436658967
H	-2.16801433731177	0.60815652283348	-0.54986085479605
H	-2.02424591589234	0.50469123059765	1.20448934847892
C	0.78592740123416	0.41931873452778	0.99287909336847
H	1.79250225128849	0.83426046308520	0.95527093764387
H	0.47778921240458	0.31718658618609	2.03642765139908
C	1.15808657755658	-0.54420190026830	-1.19191906891383
H	2.24844764077995	-0.51003242763808	-1.20903945317797
H	0.80998428732513	-1.25500514886176	-1.94153418605727
H	1.15084274894851	-1.74965578103949	0.63721206908512
H	-0.38957172177946	2.25456239875890	0.68550431184647
C	0.58786217815262	0.79047820355978	-1.39929491125837
C	0.04509012626675	1.91368974974145	-1.41380655436137

G–E(el) = 0.12746686 Hartree
Final single point energy E(CCSD(T)) = -310.143409653487 Hartree

Transition state TSb

Charge = 0, Multiplicity = 1

C	-0.90482055533927	-1.06237420329080	0.14532384200895

C	0.61796389508564	-0.81263815727309	0.15352314992145
C	-0.30579658328643	1.26071866742664	0.35300771403134
C	-1.53497322799856	0.33657742136984	0.38307537360578
H	-1.22925330678227	-1.50554287026895	-0.79609492484374
H	-1.17610176968376	-1.75066847004597	0.94508882405055
H	-2.26696487114574	0.60836703593690	-0.37446863328081
H	-2.01245514987788	0.39568737628243	1.36155985325923
C	0.75547943982568	0.40106888923096	1.07549086454757
H	1.74839865903614	0.84854665088145	1.06045729402312
H	0.45768485216822	0.18730659238724	2.10294569630376
C	1.13068677480944	-0.40028251018916	-1.24397065151077
H	2.21480243342645	-0.34014010796246	-1.24997673427749
H	0.77571175464666	-1.10664577272682	-1.98774945000803
H	1.18633732855749	-1.68827508946558	0.46823970790092
H	-0.45732597688180	2.26389345378144	0.74464013010894
C	0.23250887582617	1.26099544178143	-1.01221627411525
C	0.76811742761383	1.10340565214449	-2.12887578172551

G–E(el) = 0.12758155 Hartree
Final single point energy E(CCSD(T)) = -310.142288532347 Hartree

2-Methylenebicyclo[2.2.1]heptane (11)

Charge = 0, Multiplicity = 1

C	2.18790816766552	-0.89713890134570	0.08551253740696
C	1.91995057815873	1.34234531486113	-0.05373840405044
C	0.47854885969045	0.80674293193669	-0.07781156012964
H	-0.08071134009307	1.12215122380556	-0.96016321758979
H	-0.07273340615939	1.13627882877751	0.80642516952705
C	2.59237779956136	0.34356238752505	0.90323991960387
H	3.67417730942152	0.47220828573331	0.96567139163506
H	2.16207603545082	0.35566104418005	1.90568001712343
C	2.79529904083752	-0.55056163757260	-1.29253148464726
H	3.85646836204450	-0.80321655817257	-1.30409222129201
H	2.30939343960476	-1.09933910247013	-2.09832898799311
C	2.58772240026562	0.98750752357843	-1.39415728612223
H	3.54232360436764	1.50370026241272	-1.49948109382714
H	1.96283552037609	1.26938063963170	-2.24216311183191
H	2.48242404888303	-1.87020091256644	0.47303726894521
H	1.99675945414421	2.39324206260046	0.21793176272846
C	0.69529897531098	-0.70059782839111	-0.03075023470216
C	-0.23181570993613	-1.64575257645151	-0.07898819822386

H	-1.28352597835435	-1.40198213260121	-0.17647539922939
H	0.03189301876016	-2.69526426547135	-0.02009699733108

G–E(el) = 0.15208028 Hartree
Final single point energy E(M06-2X) = -312.016814072611 Hartree

Bicyclo[3.2.1]octane (S1)

Charge = 0, Multiplicity = 1

C	0.04929920775039	0.23927960975764	-0.31136829476866
C	1.58426296126582	0.30097803823386	-0.44513363973454
C	0.96395057725987	2.34948547062035	0.56307318686534
C	-0.35801304951015	1.58455351168196	0.35083207848367
H	-0.43288133405875	0.08987697350365	-1.27918704393245
H	-0.23728080469277	-0.59856978092786	0.32519069430317
H	-1.05904043313409	2.15395639778629	-0.26219568795015
H	-0.84254940151806	1.40285420015434	1.31087410807479
C	1.97161532664888	1.20662099884062	0.72926139941112
H	3.00999737071334	1.54253281055954	0.68451869600429
H	1.81561742033748	0.69097888083202	1.68063180568672
C	2.00930830231960	0.97421849570864	-1.75597545531232
H	3.09397211740391	1.12063998424896	-1.73976827855887
H	1.78695513436112	0.32066689206091	-2.60351898588961
H	2.03670195451300	-0.68945836619101	-0.37618817271641
H	0.91990611677981	2.99861950522932	1.43891433664963
C	1.34358373648716	3.17381241739872	-0.67347315932504
H	2.34933332276156	3.58084268467167	-0.52868982089194
H	0.66573906562616	4.02473163627988	-0.78027218662458
C	1.30650891590353	2.32215012952406	-1.94644414608465
H	1.75370803734084	2.86752765124427	-2.77970565879404
H	0.26376340544136	2.14294329878217	-2.22362986489544

G–E(el) = 0.17781962 Hartree
Final single point energy E(CCSD(T)) = -312.711665651222 Hartree

Cycloheptyne (S2)

Charge = 0, Multiplicity = 1

C	-3.12995260584736	-1.58048481231175	-0.18677960487602
C	-1.64447248070347	-1.30937116315975	0.15965948059896
C	-1.16828208103952	0.15279012090176	-0.02592000118775

C	-3.84080491261320	-0.43328282540733	0.38650829546289
C	-1.43603985100006	1.14383719868069	1.13376712566659
C	-3.74630423232416	0.68082374467942	0.82952697396734
C	-2.84390040720888	1.79025206570944	1.15361867974896
H	-3.27428595957118	-1.60577315593464	-1.26929702045728
H	-1.47750863216173	-1.59846755899415	1.20057550960387
H	-1.58289376998344	0.55692020961992	-0.95564612530213
H	-1.28806491174127	0.61709663640137	2.08015121747774
H	-3.45376004053811	-2.54303306019627	0.20876122872657
H	-1.02482142444191	-1.96552940090945	-0.45608865204681
H	-0.08620054171319	0.11622239291142	-0.16526287479225
H	-0.69309597689500	1.94397289934192	1.09563166098019
H	-3.04563242675126	2.25584841553938	2.11819608824603
H	-2.92086856546622	2.56884120312801	0.39131902818307

G–E(el) = 0.12238291 Hartree
Final single point energy E(CCSD(T)) = -272.167216565915 Hartree

Cyclopheptane (S3)

Charge = 0, Multiplicity = 1

C	-2.86142061898079	-0.81924141868910	-0.01063586889843
C	-1.33137313930543	-0.78795979874426	-0.03077333649573
C	-0.69562550597206	0.59949974155011	0.01761426501508
C	-3.45411864208615	-0.42382686313086	1.34639286467094
C	-1.16207055291091	1.50547956488638	1.15985939464558
C	-3.68748813791019	1.07685299836108	1.55094083516196
C	-2.60233857032739	1.99983662555531	0.98634099508293
H	-3.26273414233773	-0.17619524726443	-0.80154199731321
H	-0.97147038860381	-1.37520282079303	0.82110458593272
H	-0.89758265319309	1.11734522810623	-0.92637042903152
H	-1.05133274083635	0.98987013603777	2.12005205349389
H	-2.78723999636448	-0.79952680579766	2.12821018487348
H	-3.79425016646654	1.26256876793839	2.62312514674998
H	-3.18017934277173	-1.83583118843547	-0.25149366490501
H	-0.97256544240001	-1.29804766545898	-0.92867203155233
H	0.38929443780683	0.47738183437714	0.07477630663115
H	-4.40659642321828	-0.93708079412986	1.49579814922859
H	-0.49503630293235	2.36958573825805	1.19753564797529
H	-4.64259024567760	1.35646214750870	1.09815756089994
H	-2.71474951443644	2.97953421226350	1.45596215442486
H	-2.77803262107549	2.15919258760101	-0.08172981659017

G–E(el) = 0.16984089 Hartree
Final single point energy E(CCSD(T)) = -274.667800137001 Hartree

Ethyl isopropyl alkylidene carbene (S4)

Charge = 0, Multiplicity = 1

C	-2.806576000000	1.073331000000	0.109848000000
C	-3.070915000000	1.952799000000	1.011302000000
C	-3.304510000000	0.805506000000	-1.284241000000
C	-2.686873000000	1.753625000000	-2.313067000000
H	-4.389689000000	0.905081000000	-1.297075000000
H	-3.076774000000	-0.229377000000	-1.545369000000
H	-3.048372000000	1.512335000000	-3.313176000000
H	-2.953416000000	2.785586000000	-2.087314000000
H	-1.599664000000	1.678933000000	-2.314375000000
C	-1.692481000000	0.205344000000	0.764151000000
C	-0.453214000000	0.213889000000	-0.125537000000
C	-2.221018000000	-1.204278000000	1.012256000000
H	-1.424112000000	0.641874000000	1.731266000000
H	-0.080460000000	1.227298000000	-0.273058000000
H	0.334308000000	-0.383845000000	0.336372000000
H	-0.676272000000	-0.220254000000	-1.102605000000
H	-3.083491000000	-1.184754000000	1.677341000000
H	-2.514105000000	-1.684683000000	0.077089000000
H	-1.440191000000	-1.813533000000	1.470956000000

G–E(el) = 0.13680870Hartree
Final single point energy E(CCSD(T)) = -273.328885616656 Hartree

2-Methylhex-3-yne (S5)

Charge = 0, Multiplicity = 1

C	-3.17073833980051	0.90135958789331	-0.83243830207210
C	-2.35958235203191	0.52267586677856	-0.02939899406564
C	-4.13665719435910	1.36434165183327	-1.82996434883408
C	-3.48426576534199	1.65177382428309	-3.18406958247495
H	-4.62875600382882	2.26513972593613	-1.45655597040679
H	-4.91680515121228	0.60887959051653	-1.94631976003310
H	-4.23174581442031	1.99359134958890	-3.89980520781377
H	-2.72069901385833	2.42287743387199	-3.08548818725839

H	-3.01082233423767	0.75356919092912	-3.57963808023277
C	-1.36480095121485	0.05279367132190	0.94180307742402
C	0.04063092245921	0.07812781277033	0.33402293457583
C	-1.71793796536745	-1.34912848559610	1.44730628731477
H	-1.38370250081877	0.74004963196937	1.79274234909166
H	0.30219147841209	1.07839597157339	-0.00965348809231
H	0.77404308548428	-0.23990713501531	1.07631434461899
H	0.09269107313029	-0.60255604560659	-0.51725289102240
H	-2.71107897686085	-1.36679383011381	1.89507454399745
H	-1.70097217579158	-2.06092948508976	0.62039184113352
H	-0.99134202034142	-1.67052332784433	2.19482242415007

G–E(el) = 0.13707935 Hartree
Final single point energy E(CCSD(T)) = -273.406138244404 Hartree

Transition state TS-et-mig

Charge = 0, Multiplicity = 1

6	-0.533673000	0.672802000	0.801381000
6	-1.354321000	1.604855000	0.631649000
6	-1.277040000	0.595389000	-0.835776000
6	-0.621784000	1.417560000	-1.923968000
1	-2.352938000	0.505753000	-0.942850000
1	-0.907334000	-0.436279000	-0.863661000
1	-0.744723000	0.927049000	-2.891943000
1	-1.063855000	2.411260000	-1.970558000
1	0.444912000	1.529835000	-1.728805000
6	0.501996000	-0.286390000	1.229288000
6	1.701833000	-0.291215000	0.279760000
6	-0.057767000	-1.694999000	1.435572000
1	0.829967000	0.100125000	2.198830000
1	2.113446000	0.710319000	0.158718000
1	2.479720000	-0.945510000	0.673779000
1	1.412962000	-0.667424000	-0.704046000
1	-0.906412000	-1.684547000	2.118028000
1	-0.382270000	-2.126986000	0.486785000
1	0.717281000	-2.341598000	1.847818000

G–E(el) = 0.13631014 Hartree
Final single point energy E(CCSD(T)) = -273.316154494244 Hartree

Transition state TS-ipr-mig

Charge = 0, Multiplicity = 1

C	-0.894497000000	0.724515000000	0.375945000000
C	-0.752086000000	1.070540000000	1.565198000000
C	-1.198852000000	0.429647000000	-1.025826000000
C	-0.538502000000	1.384497000000	-2.021479000000
H	-2.285918000000	0.468714000000	-1.127663000000
H	-0.918457000000	-0.607007000000	-1.232476000000
H	-0.824023000000	1.119531000000	-3.039220000000
H	-0.853791000000	2.408961000000	-1.828446000000
H	0.546874000000	1.342435000000	-1.944689000000
C	0.488226000000	-0.238369000000	1.346417000000
C	1.568869000000	-0.173896000000	0.276360000000
C	-0.105697000000	-1.615621000000	1.543265000000
H	0.942740000000	0.095734000000	2.272829000000
H	1.914196000000	0.848888000000	0.130103000000
H	2.415073000000	-0.777467000000	0.611727000000
H	1.238469000000	-0.576309000000	-0.681930000000
H	-0.818589000000	-1.614945000000	2.366020000000
H	-0.617450000000	-1.964096000000	0.643969000000
H	0.693417000000	-2.325751000000	1.769896000000

G–E(el) = 0.13642512 Hartree
Final single point energy E(CCSD(T)) = -273.310388501644 Hartree

Nudged Elastic Band (NEB-TS) settings

Method type .... climbing image
Threshold for climbing image .... 2.00e-02 Eh/Bohr
Free endpoints .... off
Tangent type .... improved
Number of intermediate images 6
Number of images free to move 6
Spring type for image distribution .... distance between adjacent images
Spring constant .... energy weighted (0.0100 -to- 0.1000) Eh/Bohr^2
Spring force perp. to the path .... none
Generation of initial path .... image dependent pair potential
Initial path via TS guess .... off

Minimization of RMSD: Rotation .... always
Minimization of RMSD: Translation type .... centroid

Center fixed to origin .... true
Remove external force .... true

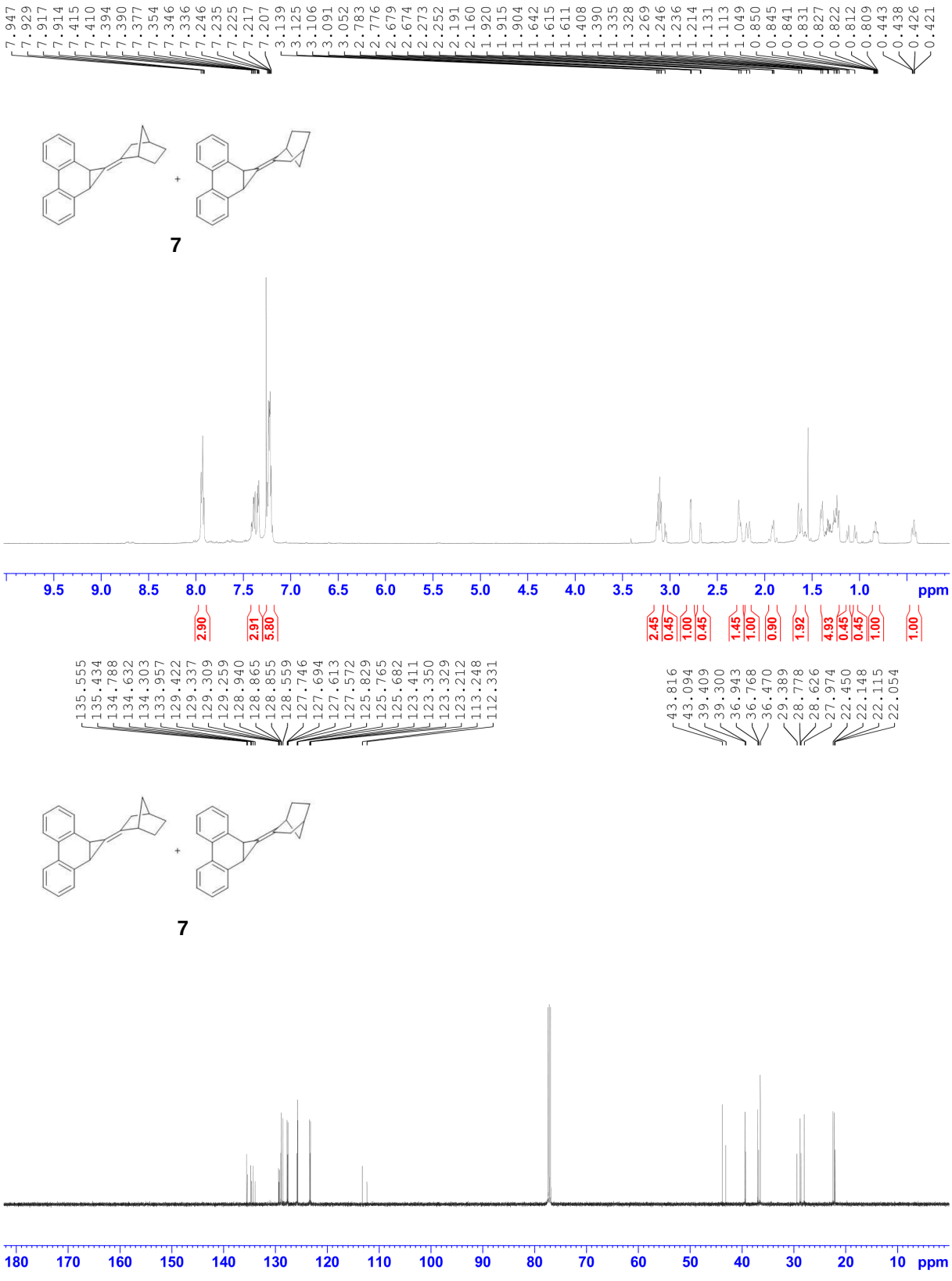
Reparametrization of the path .... off
Convergence thresholds:
Convergence monitored for .... all images
Scaling factor 10.00

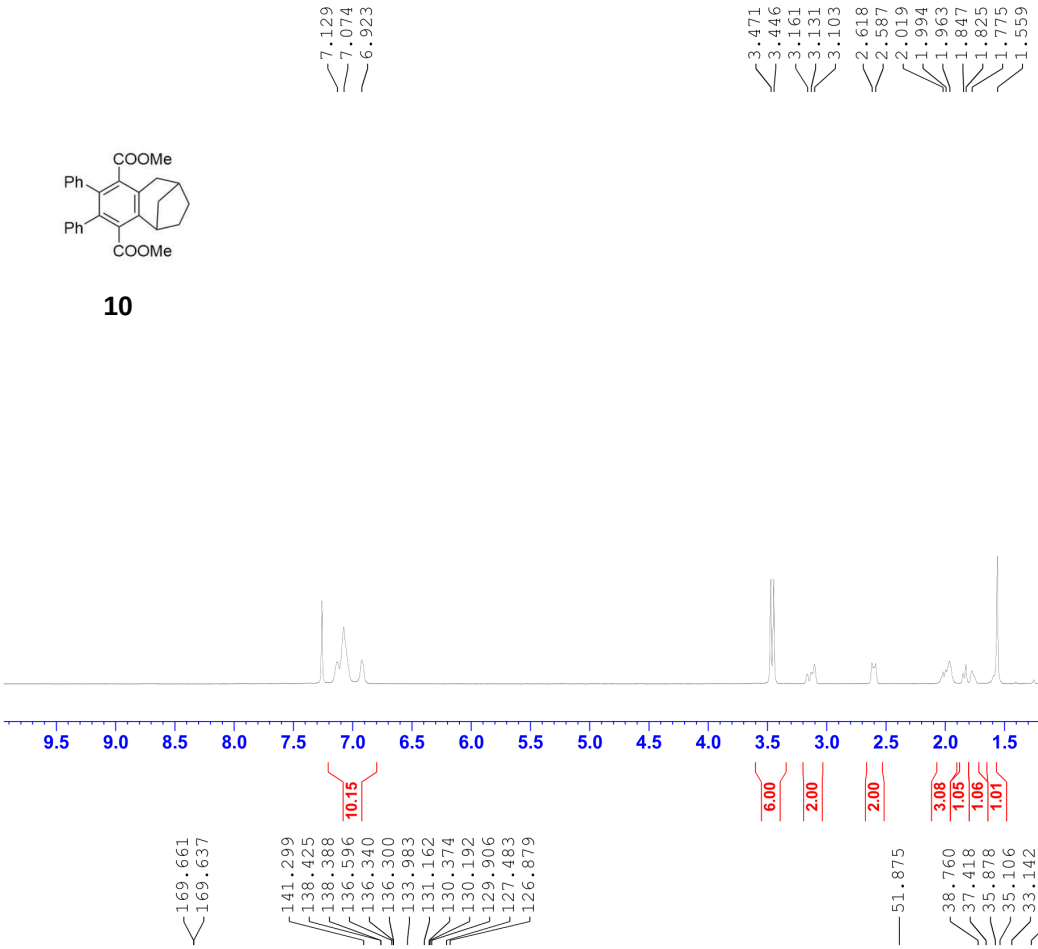
Convergence parameters for regular images:
Max(|Fp|) .... 2.00e-02 Eh/Bohr
RMS(Fp) .... 1.00e-02 Eh/Bohr

Convergence parameters for climbing image:
Max(|F|) .... 2.00e-03 Eh/Bohr
RMS(F) .... 1.00e-03 Eh/Bohr
Optimization method:
Method .... L-BFGS
Max. iterations 500
Step size 1.00
Maximum allowed step size .... 0.10 Bohr

LBFGS parameters:
Memory 20
Initial step size 0.0010
Estimate curvature .... YES
Reset on maxmove .... YES
Reparam. on reset .... NO

Experimental Spectra.

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3.131
3.103
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2.587
2.019
1.994
1.963
1.847
1.825
1.775
1.559
COOMe
Ph
Ph
COOMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
10.15
6.00
2.00
2.00
3.08
1.05
1.06
1.01
169.661
169.637
141.299
138.425
138.388
136.596
136.340
136.300
133.983
131.162
130.374
130.192
129.906
127.483
126.879
51.875
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35.878
35.106
33.142
29.860
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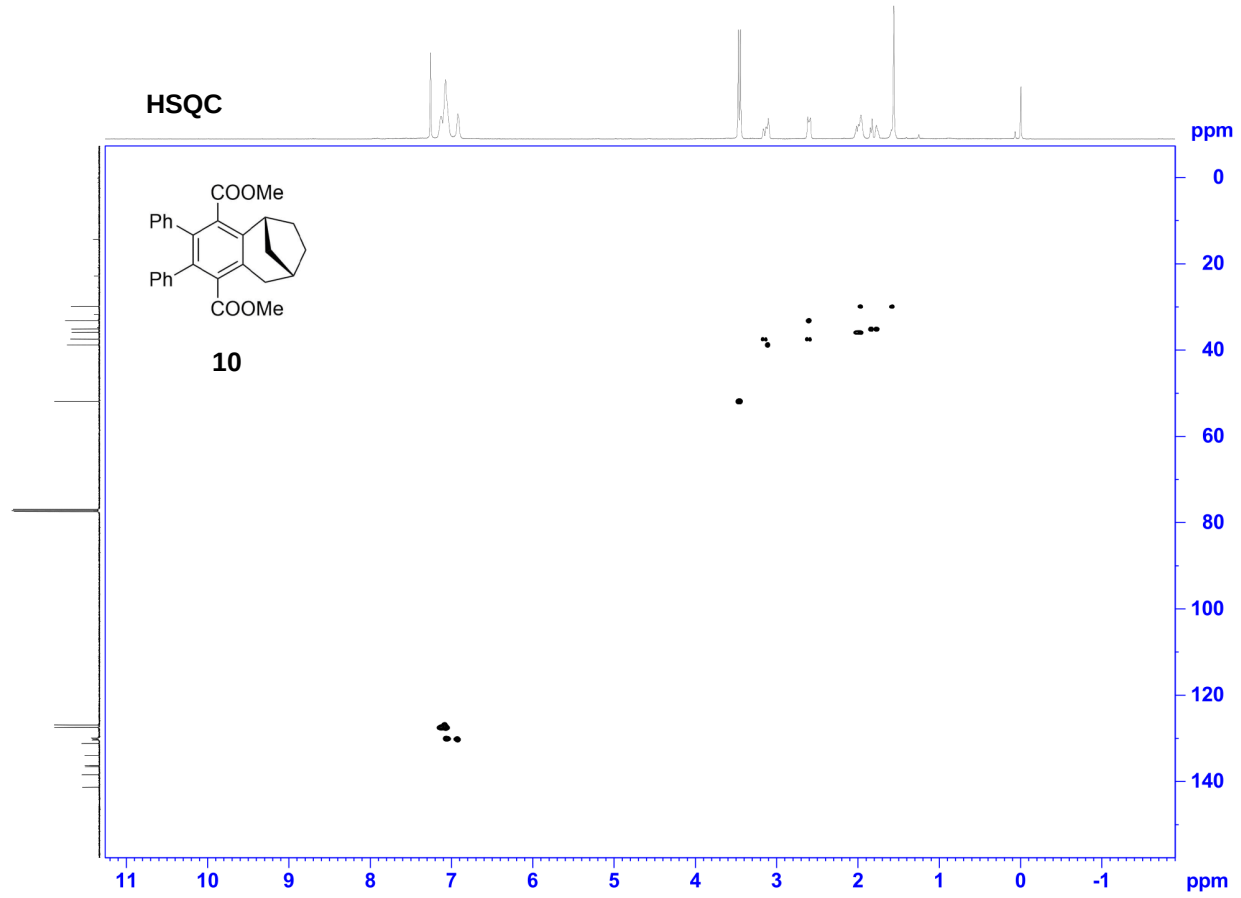
10

10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COOMe
Ph
Ph
COOMe
10
ppm
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120
140
11
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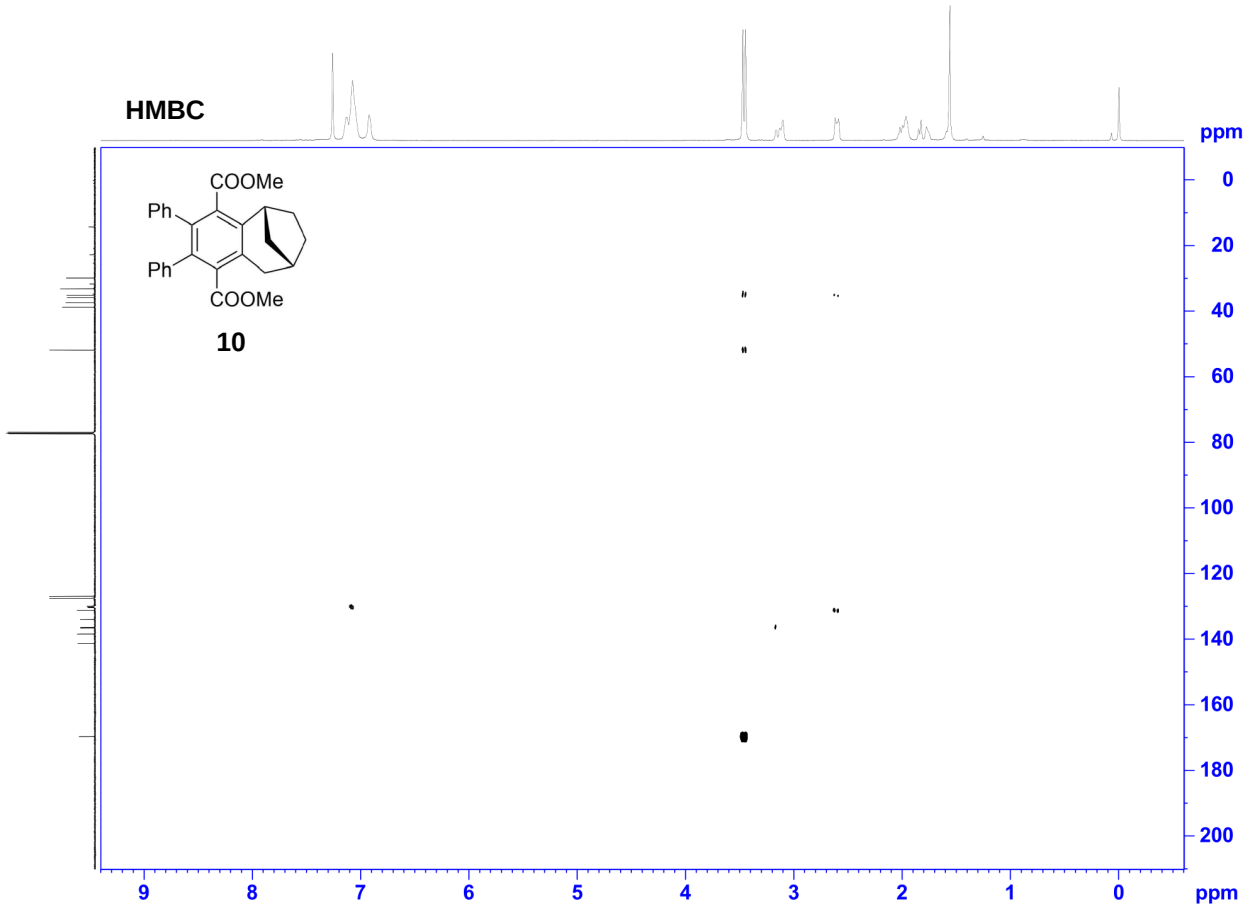
7
6
5
4
3
2
1
0
-1
ppm


HMBC
COOMe
Ph
Ph
COOMe
10
ppm
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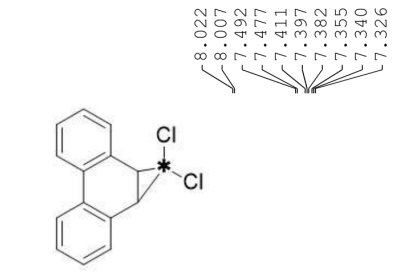
20
40
60
80
100
120
140
160
180
200
9
8
7
6
5
4
3
2
1
0
ppm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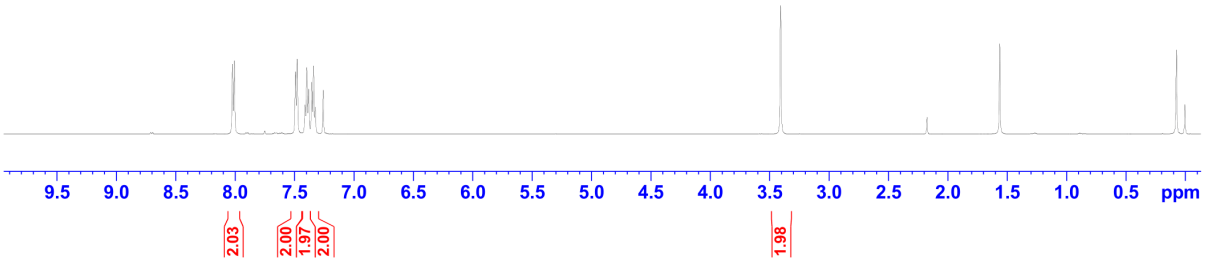
8.007
7.492
7.477
7.411
7.397
7.382
7.355
7.340
7.326
3.407
Cl
Cl

6*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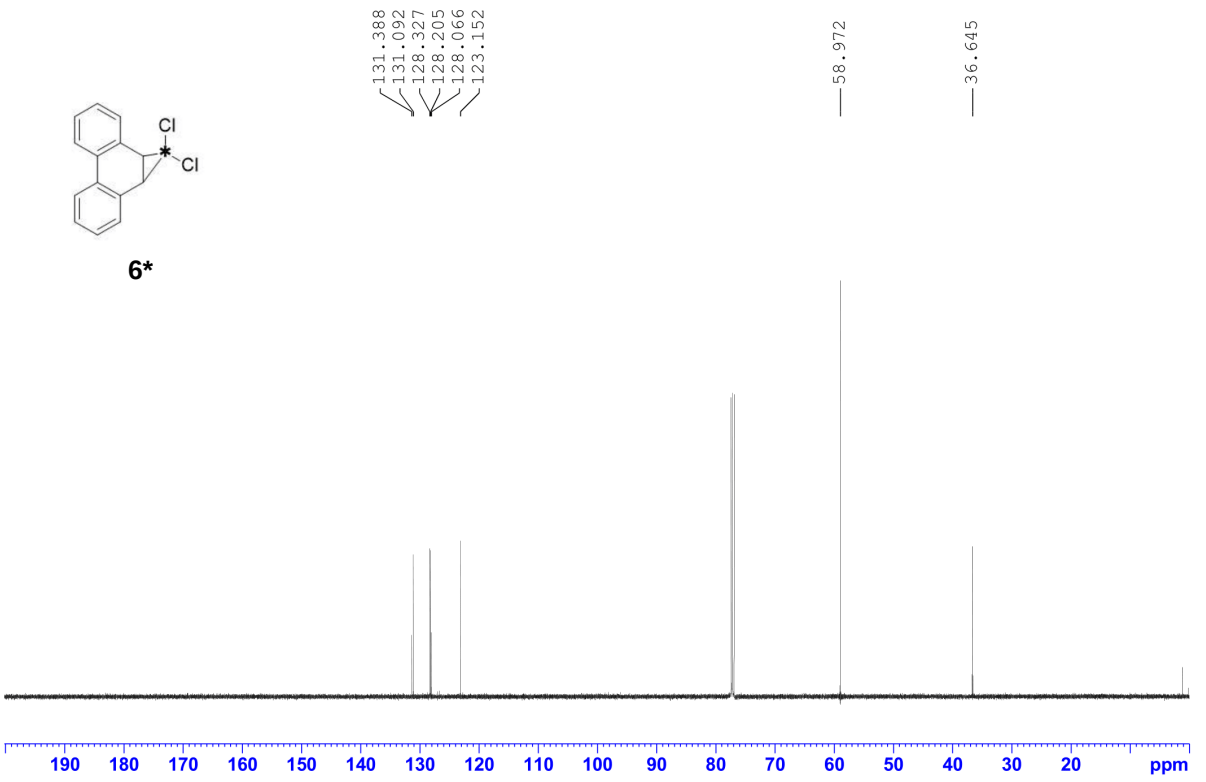
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
2.00
1.97
2.00
1.98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128.066
123.152
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36.645
Cl
Cl
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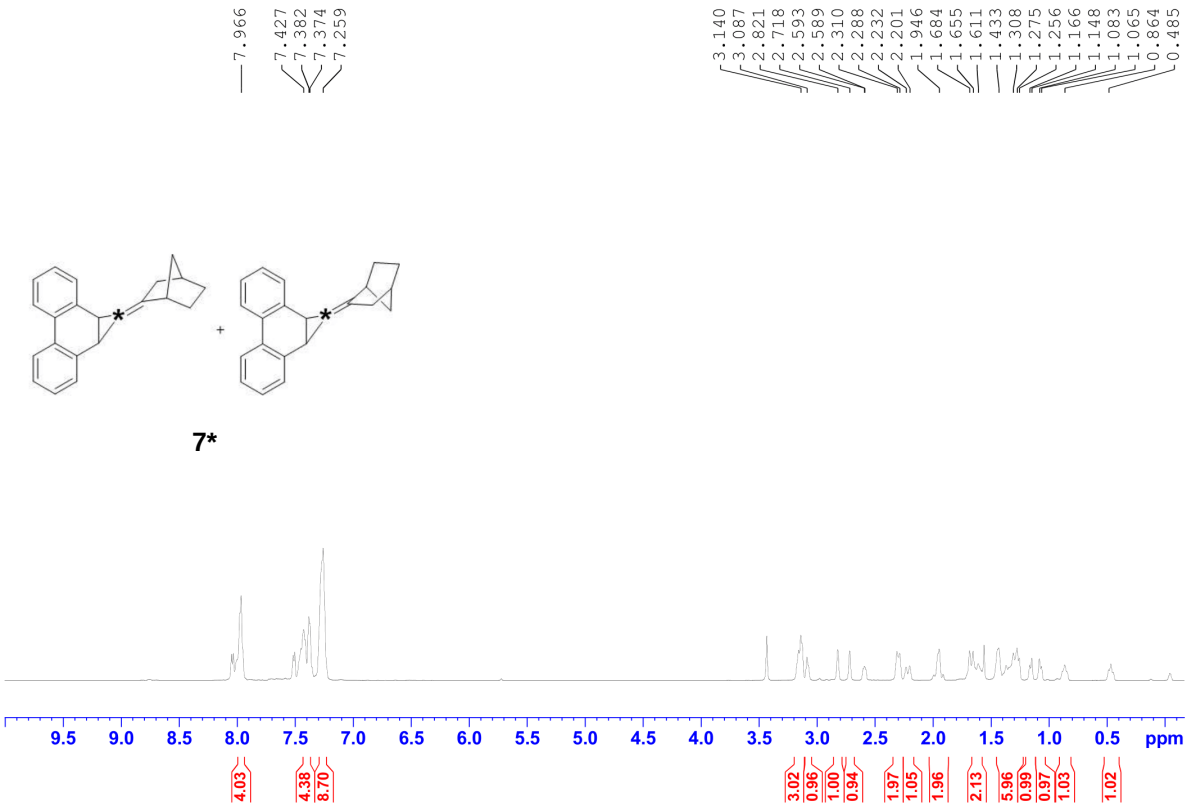
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

6*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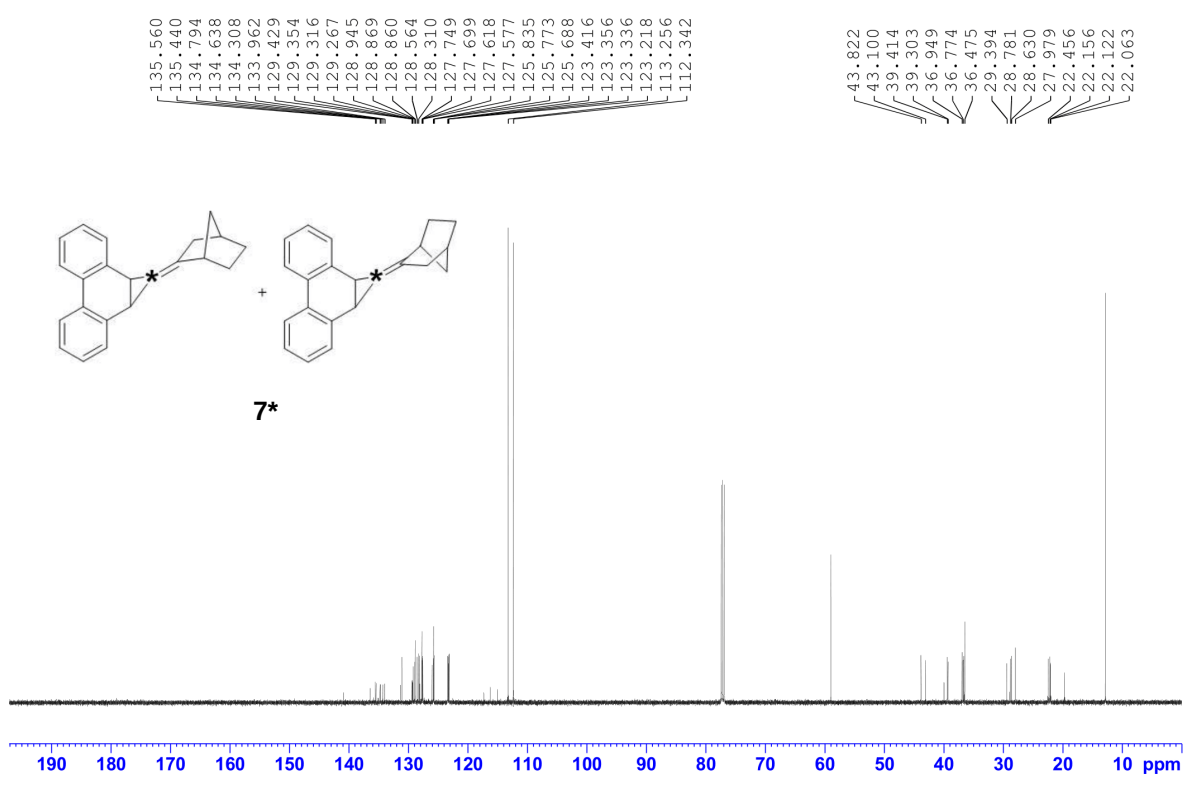
2.593
2.589
2.310
2.288
2.232
2.201
1.946
1.684
1.655
1.611
1.433
1.308
1.275
1.256
1.166
1.148
1.083
1.065
0.864
0.485
7*
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.03
4.38
8.70
3.02
0.96
1.00
0.94
1.97
1.05
1.96
2.13
5.96
0.99
0.97
1.03
1.02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128.564
128.310
127.749
127.699
127.618
127.577
125.835
125.773
125.688
123.416
123.356
123.336
123.218
113.256
112.342
43.822
43.100
39.414
39.303
36.949
36.774
36.475
29.394
28.781
28.630
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22.456
22.156
22.122
22.063
7*
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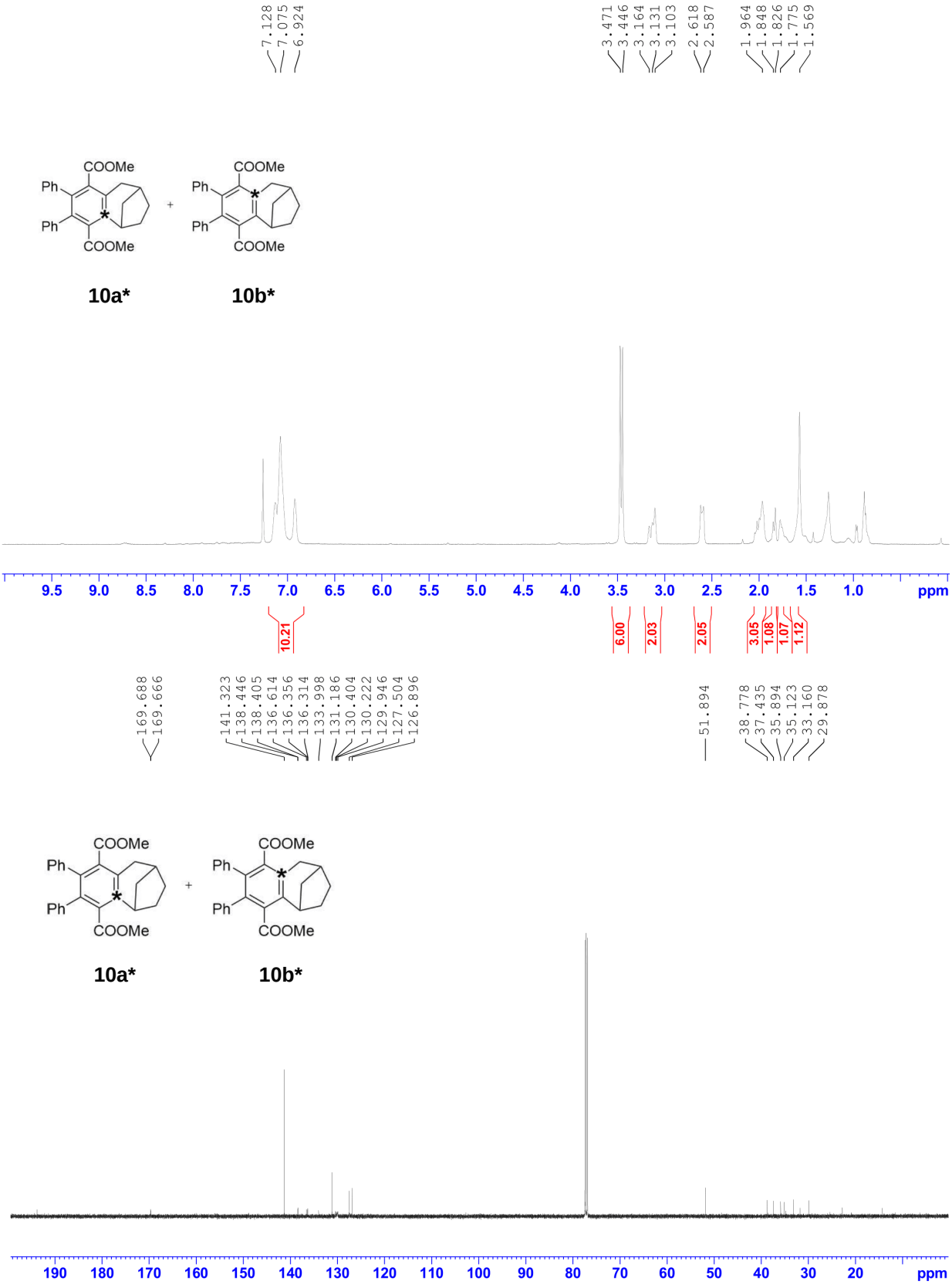
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7.075
6.924
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2.587
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1.826
1.775
1.569
COOMe
Ph
Ph
COOMe
10a*
10b*
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
10.21
6.00
2.03
2.05
3.05
1.08
1.07
1.12
169.688
169.666
141.323
138.446
138.405
136.614
136.356
136.314
133.998
131.186
130.404
130.222
129.946
127.504
126.896
51.894
38.778
37.435
35.894
35.123
33.160
29.878
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

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