Electronic Supplementary Information

β-Phenyl Quenching of 9-Phenylphenalenone. A novel Photocyclisation Reaction with Biological Implications

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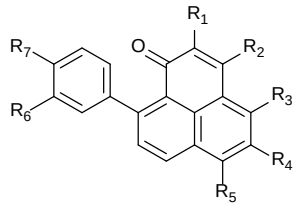
Naturally occurring 9-phenylphenalenones.



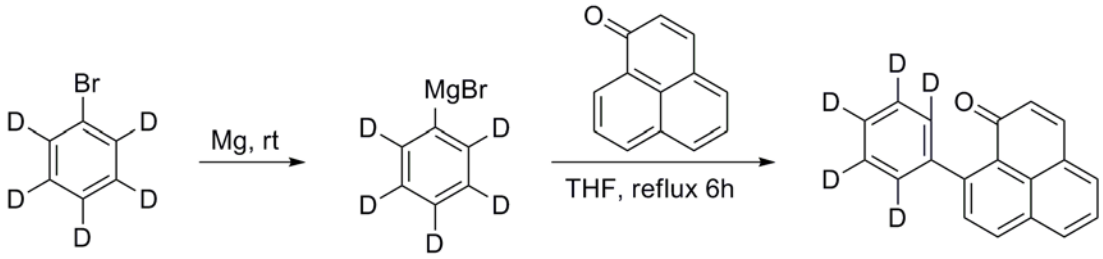
R_1	R_2	R_3	R_4	R_5	R_6	R_7	Ref.
H	H	H	H	H	H	H	[1]
OH	H	H	H	H	H	H	[2]
OMe	H	H	H	H	H	H	[3]
OH	H	H	H	H	H	OH	[2]
OH	H	H	H	H	H	OMe	[1]
OMe	H	H	H	H	H	OH	[4]
OMe	H	H	H	H	H	OMe	[4]
OH	H	H	H	H	OH	OH	[5]
OH	H	H	H	H	OMe	OH	[1]
OMe	H	H	H	H	OMe	OMe	[4]
OH	OH	H	H	H	H	OH	[1]
OH	H	OH	H	H	H	H	[6]
OH	H	OH	H	H	H	OH	[7]
OH	H	OH	H	H	OH	OH	[7]
OMe	H	OH	H	H	H	H	[1]
OMe	H	Glu	H	H	H	H	[7]
OH	H	OH	OMe	H	H	H	[5]
OH	H	H	OH	OH	H	H	[8]
OMe	H	H	OH	OH	H	H	[8]
OH	H	H	OMe	OH	H	H	[7]
OH	H	H	OH	GluGlu	H	H	[9]
OMe	H	H	OMe	OH	H	H	[10]
O-GlucGluc	H	H	OMe	OH	H	H	[11]
O-Celobiose	H	H	OMe	OH	H	H	[9]
OH	H	H	H	OH	H	H	[8]

Scheme S1: Naturally-occurring 9-phenylphenalenones. Glu = O-Glucoside.

Synthesis

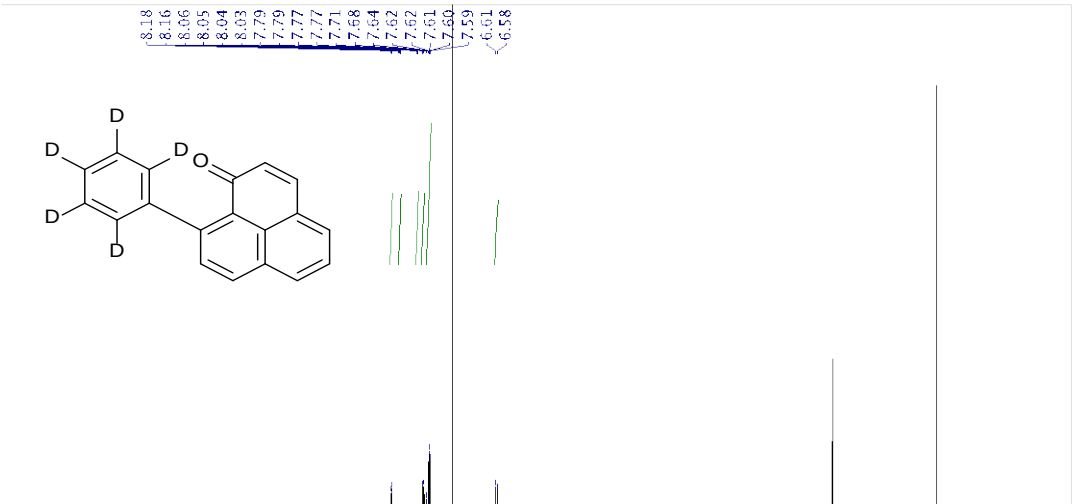
General Information. Materials obtained from commercial suppliers were used without further purification. Reactions were monitored by analytical thin-layer chromatography (TLC) (Macherey-Nagel (MN) Silicagel Polygram UV_{254} of 0,20 mm) using ultraviolet light (254nm) for visualization. Purification of products was conducted by flash column chromatography on silica gel (200−300 mesh). ^{1}H-NMR spectra were recorded on a Varian 400 spectrometer (400 MHz) using residual solvent (δ ($CDCl_3$) = 7.26) as internal standard. All of the coupling constants are reported in hertz. ^{13}C-NMR spectra were recorded on the same instrument, and chemical shifts were measured relative to solvent resonances (δ ($CDCl_3$) = 77.0). The UV-Vis spectra were recorded using a Cary 6000i spectrophotometer.

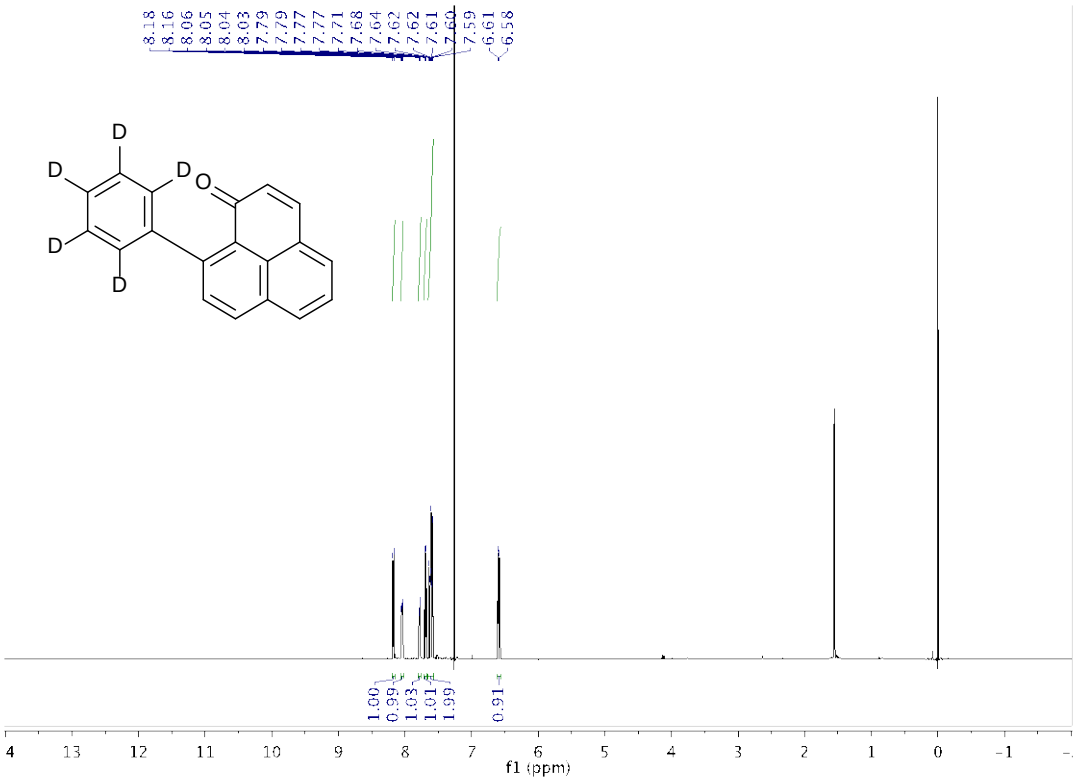
9-(Perdeuterophenyl)-1*H*-phenalen-1-one (1d).



A solution of perdeutero-bromobenzene (354 mg, 2.19 mmol, 0.7M) in diethyl ether (3 mL) was added dropwise to a suspension of magnesium turnings (78 mg, 3.2 mmol) in diethyl ether (2 mL). The reaction mixture was stirred and heated at reflux for 20 min and then cooled to room temperature. The Grignard's reagent was added to a stirred solution of phenalen-1*H*-one (284 mg, 1.58 mmol) in THF (12 mL). The reaction mixture was stirred and heated

at reflux for 6 h. The reaction mixture was cooled to room temperature, and then quenched with an aqueous saturated solution of NH_4Cl (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic extracts were washed with H_2O, brine (15 mL) and dried (Na_2SO_4). Removal of solvent under vacuo followed by silica gel column flash chromatography (EtOAc: hexanes, 1:3) afforded compound **1d** (96 mg, 24%) as a yellow solid. ^{1}H-NMR: δ 8.17 (1H, d, *J* = 8.0 Hz, H-7), 8.04 (1H, dd, *J* =1.0, 8.0 Hz, H-6), 7.78 (1H, dd, *J* = 1.0, 7.0 Hz, H-4), 7.69 (1H, d, *J* = 9.5 Hz, H-3), 7.62 (1H, dd, *J* = 7.0, 8.0 Hz, H-5), 7.60 (1H, d, *J* = 8.0Hz, H-8), 6.59 (1H, d, *J* = 9.5Hz, H-2). ^{13}C-NMR: δ 185.93 (C-1), 147.78 (C-9), 140.54 (C-3), 133.87 (C-7), 131.90 (C-9a), 131.88 (C-6), 131.77 (C-8), 131.55 (C-4), 130.68 (C-2), 128.67 (C-3a), 128.53 (C-9b), 126.52 (C-6a), 126.20 (C-5). GC-MS (EI, 70 eV): M/Z (%; fragment) 261 (24; M^+), 260 (27; M^+-H), 260 (100; M^+-D), 230 (11; M^+ -H - COH).

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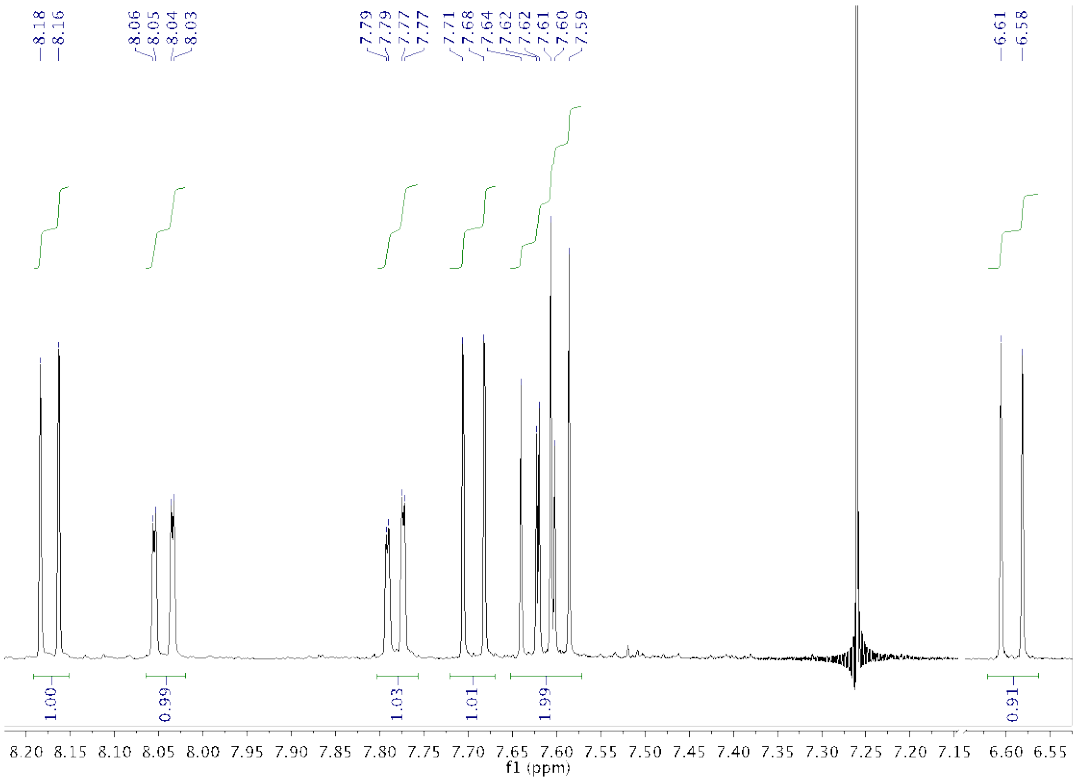
8.16
8.06
8.05
8.04
8.03
7.79
7.79
7.77
7.77
7.71
7.68
7.64
7.62
7.62
7.61
7.60
7.59
6.61
6.58
D
D
D
D
D
O
1.00
0.99
1.03
1.01
1.99
0.91
f1 (ppm)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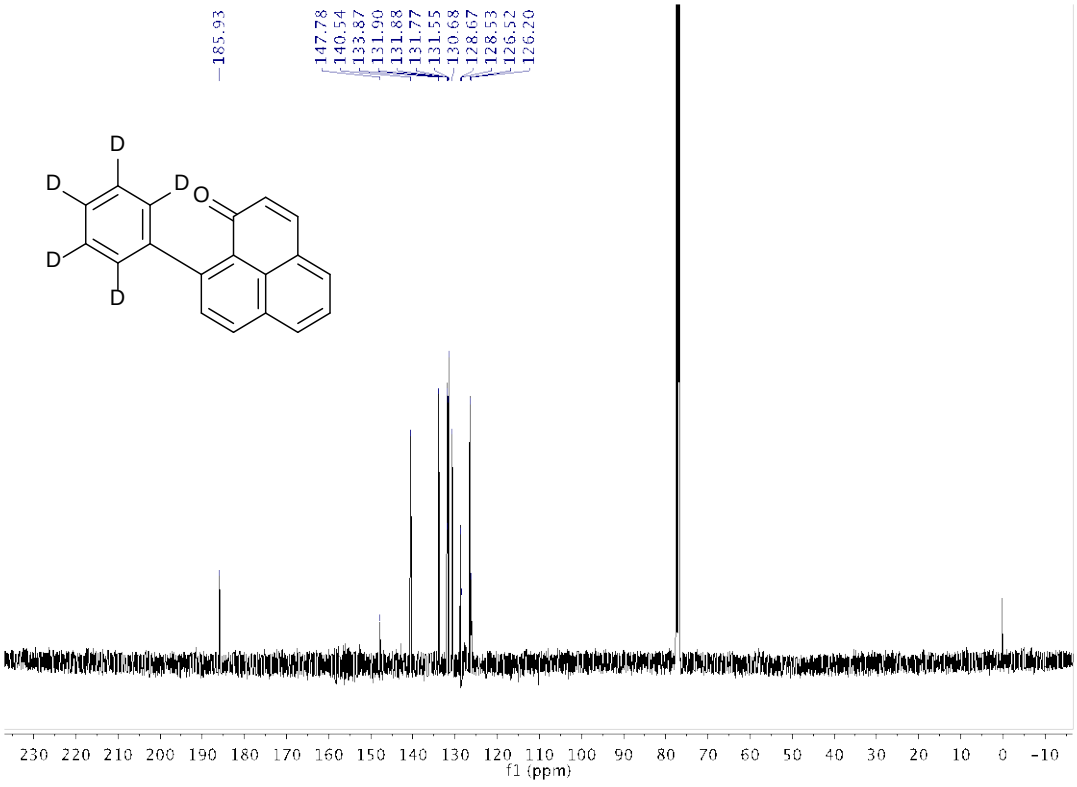
8.16
8.06
8.05
8.04
8.03
7.79
7.79
7.77
7.77
7.71
7.68
7.64
7.62
7.62
7.61
7.60
7.59
6.61
6.58
1.00
0.99
1.03
1.01
1.99
0.91
f1 (ppm)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140.54
133.87
131.90
131.88
131.77
131.55
130.68
128.67
128.53
126.52
126.20
D
D
D
D
D
O
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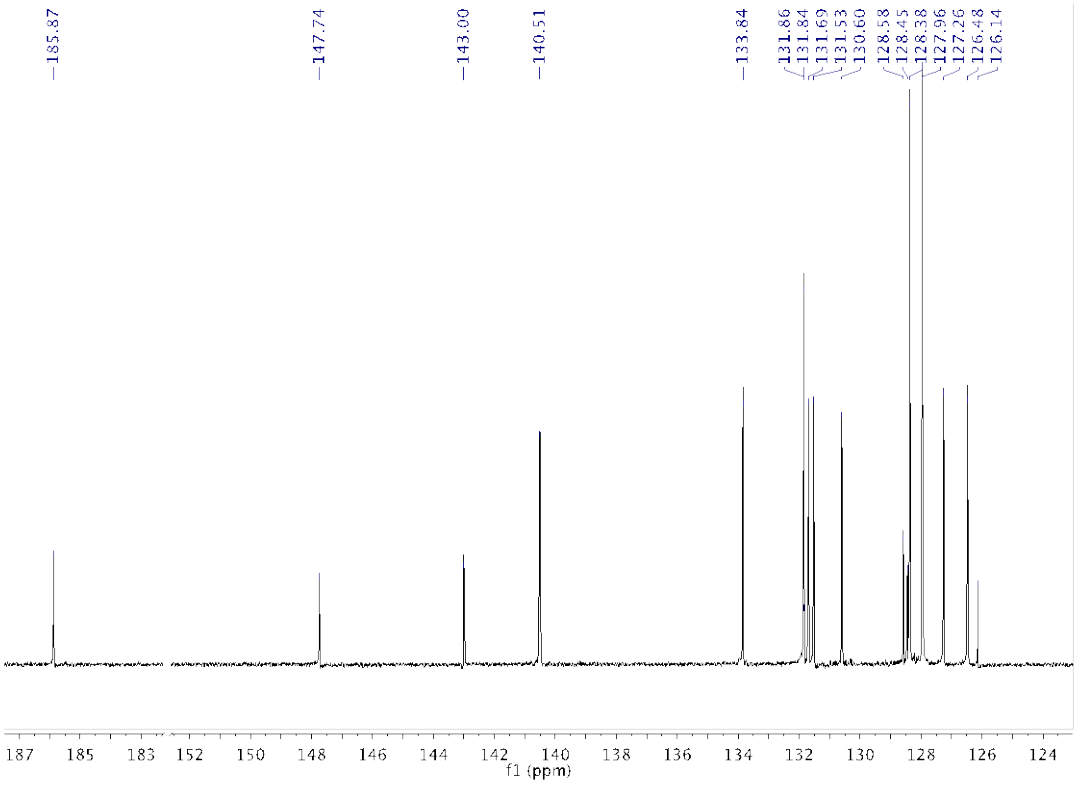
f1 (ppm)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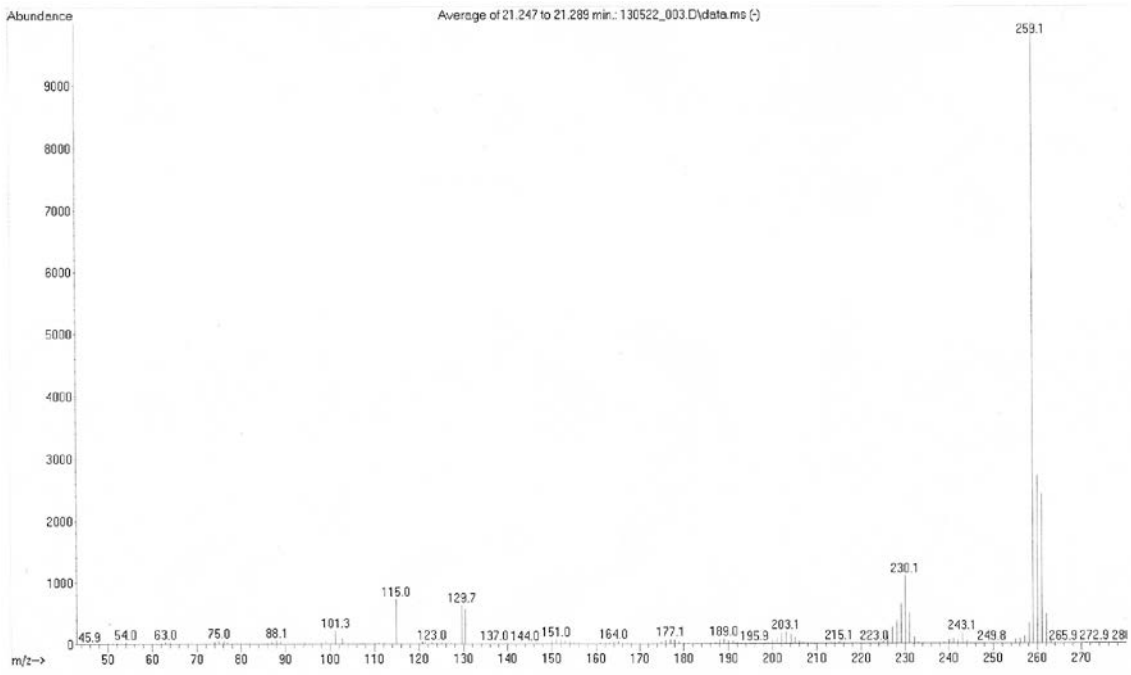
f1 (ppm)


Abundance
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259.1
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
230.1
115.0
129.7
101.3
45.9
54.0
63.0
75.0
88.1
123.0
137.0
144.0
151.0
164.0
177.1
189.0
195.9
203.1
215.1
223.0
243.1
249.8
265.9
272.9
m/z-->
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270

Spin angular momentum vs. C-O distance for *ipso*- and *ortho*-addition in ^{3}1a*.

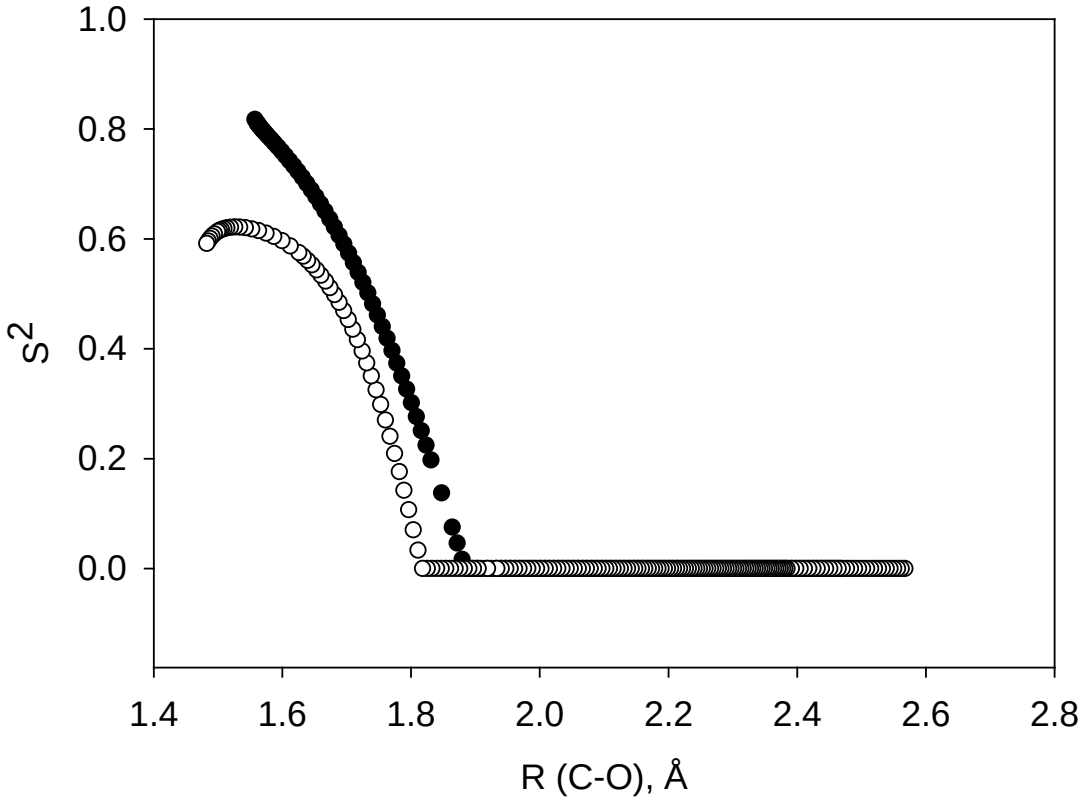

Figure S1: Plot of S^2 vs. R (C-O) for IRC of *ipso*-addition (black circles) or IRC of *ortho*-addition (light circles) of ^{3}**1a**.

ESR Spectra

ESR experiments were performed using a Bruker ElexSys E 500 ESR spectrometer. The ESR spectrum was simulated using Bruker Xsophe simulation software. Lamp photolysis of a deoxygenated solution of TCNE and **1a** in benzene yielded a brownish-yellow solution whose ESR spectrum at ambient temperature is shown in Figure S2A. The overall shape (complex multiplet of a quintet) is consistent with radical **5a**.[12] The spectrum was not observed if air was allowed into the sample. When acetonitrile was used as solvent, the ESR spectrum of the photolysis product showed the characteristic nonet signal of TCNE radical anion with g = 2.0026 and a line spacing of 1.56 Gauss (Figure S2B).

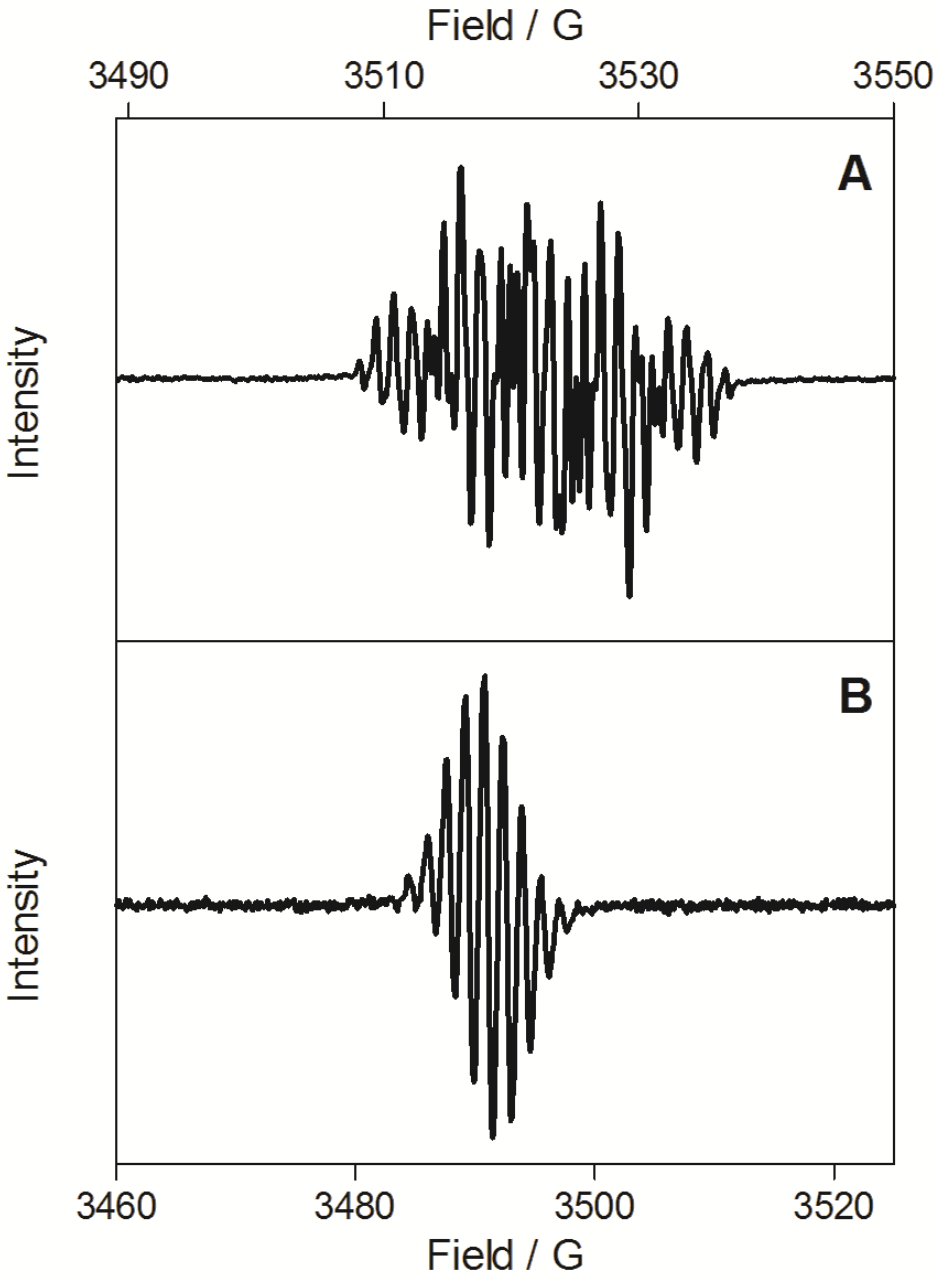

Figure S2: ESR spectrum, recorded after 10 min. photolysis of a deoxygenated solution of **1a** and TCNE in (A) benzene and (B) acetonitrile at ambient temperature.

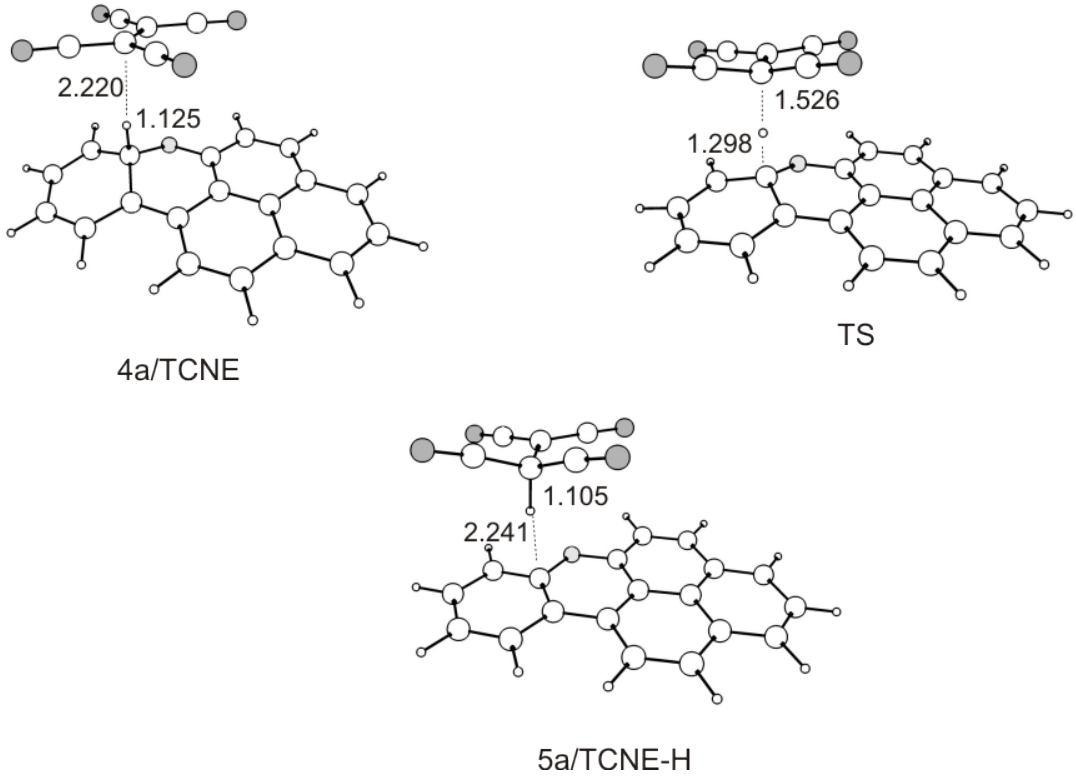

Figure S3: Geometries of the **4a**/TCNE complex, the transition state, and the **5a**/TCNE-H complex

ESI Bibliography:

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Optimized geometry (B3LYP/6-31G*) of 9-phenylphenalenone **1a**.

C	-0.28453900	-2.02179700	0.04358300
C	1.02904300	-2.42510400	0.08630300
C	2.07514100	-1.47248500	0.08008900
C	1.73487200	-0.08799400	0.00238600
C	0.36320500	0.32220000	-0.05921100
C	-0.65031600	-0.65055700	-0.01233500
H	3.67405200	-2.92528500	0.20263300
H	-1.07926800	-2.76085900	0.07688000
H	1.27651100	-3.48273100	0.13860600
C	3.43909400	-1.86535300	0.14498500
C	2.79895800	0.87139800	-0.01426300
C	4.11907000	0.44415100	0.05614700
C	4.44477900	-0.92416700	0.13542500
H	4.91402500	1.18611800	0.04698900
H	5.48571100	-1.22964000	0.18691800
C	2.47575200	2.28017400	-0.10801800
C	1.20118700	2.70801300	-0.21145400
H	3.30080800	2.99012800	-0.10494300
H	0.94867400	3.75992200	-0.30238600
C	0.05815500	1.78105500	-0.23887800
O	-1.07800600	2.21575900	-0.42256800
C	-2.11806800	-0.37496000	0.01674300
C	-2.94633000	-0.92442400	-0.97146600
C	-2.71082100	0.31603700	1.08438200
C	-4.33211800	-0.76398900	-0.91117600
H	-2.50012900	-1.46440600	-1.80274700
C	-4.09290500	0.46144500	1.15340900
H	-2.08137700	0.74125900	1.86019600
C	-4.90983900	-0.07391200	0.15316400
H	-4.95688000	-1.18308300	-1.69562000
H	-4.53541700	0.99749700	1.98886600
H	-5.98858800	0.04662500	0.20627400

E(B3LYP/6-31G(d)): -806.4873976
E(B3LYP/6-31G(d) + ZPE): -806.236566
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.7571401
No vibrational mode with imaginary frequency.

Optimized geometry (B3PW91/6-31G*) of 9-phenylphenalenone **1a**.

C	-0.28432500	-2.01940800	0.03744900
C	1.02818500	-2.42159700	0.07973800
C	2.07160700	-1.46909300	0.07675000
C	1.73094400	-0.08751900	0.00104700
C	0.36264100	0.32086300	-0.06284700
C	-0.64844400	-0.65056200	-0.01693400
H	3.67004800	-2.92025600	0.19874700
H	-1.08019300	-2.75829300	0.07052600
H	1.27627000	-3.47953900	0.13045500
C	3.43343000	-1.86017400	0.14324800
C	2.79081300	0.87183200	-0.00997900
C	4.10986400	0.44716900	0.06267700
C	4.43682900	-0.91868000	0.13844300
H	4.90388600	1.19081300	0.05823300
H	5.47826300	-1.22333300	0.19148800
C	2.46619700	2.27765600	-0.09891200
C	1.19207600	2.70292300	-0.20623800
H	3.28967500	2.99001100	-0.08959700

H	0.93873800	3.75524700	-0.29517600
C	0.05453600	1.77445900	-0.24629900
O	-1.07913900	2.20222600	-0.44483600
C	-2.11138500	-0.37393900	0.01590900
C	-2.94110200	-0.91781400	-0.97103200
C	-2.69816900	0.31061700	1.08805600
C	-4.32440400	-0.75670200	-0.90532300
H	-2.49676700	-1.45278300	-1.80720400
C	-4.07806800	0.45635800	1.16204800
H	-2.06478000	0.73000400	1.86454800
C	-4.89719900	-0.07239600	0.16300400
H	-4.95247000	-1.17093600	-1.69011700
H	-4.51774900	0.98843100	2.00191700
H	-5.97595700	0.04887300	0.22004500

E(B3PW91/6-31G(d)): -806.177967
E(B3PW91/6-31G(d) + ZPE): -805.926477
E(B3PW91/cc-pVTZ//B3PW91/6-31G(d)): -806.4309986
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) of the first excited triplet state of 9-phenylphenalenone, **^{3}1a***.

C	-0.27777100	-2.05210400	-0.04885200
C	1.05486400	-2.43838100	0.01978400
C	2.08874900	-1.47277400	0.07547600
C	1.72881000	-0.08232800	-0.00281400
C	0.36812700	0.30158100	-0.11917800
C	-0.66961400	-0.70849500	-0.07404800
H	3.70695800	-2.88871900	0.23486200
H	-1.05042600	-2.81498000	-0.02142000
H	1.31432800	-3.49250300	0.07011500
C	3.44592900	-1.83515400	0.18633200
C	2.78197300	0.90887000	0.01530900
C	4.14964200	0.47918000	0.14543800
C	4.46279600	-0.85468300	0.22813900
H	4.92766000	1.23702700	0.16829200
H	5.49964600	-1.16620600	0.32113800
C	2.45567800	2.26962400	-0.09238300
C	1.13437600	2.66338100	-0.25003400
H	3.24998100	3.01079000	-0.05838500
H	0.86406500	3.70610500	-0.38362600
C	0.06699000	1.71694900	-0.33048300
O	-1.10004600	2.12806300	-0.64908900
C	-2.11605800	-0.40746800	0.01135400
C	-3.03258800	-1.11378400	-0.78913800
C	-2.62691500	0.50292800	0.95951800
C	-4.40384500	-0.90534400	-0.66296600
H	-2.65874000	-1.80670300	-1.53787400
C	-3.99852700	0.69973100	1.09379200
H	-1.94233000	1.03645800	1.61008700
C	-4.89358300	0.00124400	0.28129200
H	-5.09197500	-1.44710200	-1.30662600
H	-4.36930300	1.40205000	1.83549300
H	-5.96368900	0.16144000	0.38143100

E(UB3LYP/6-31G(d)): -806.4227339
E(UB3LYP/6-31G(d) + ZPE): -806.175129
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.691048
No vibrational mode with imaginary frequency.

Optimized geometry (UB3PW91/6-31G*) of the first excited triplet state of 9-phenylphenalenone, **^{3}1a***.

C	-0.27105000	-2.05570400	-0.04808500
C	1.06146500	-2.43560600	0.02167800
C	2.08958800	-1.46655700	0.07686100
C	1.72550900	-0.08074000	-0.00288700
C	0.36562600	0.29545200	-0.11993300
C	-0.66504500	-0.71483300	-0.07378100
H	3.71290100	-2.87505600	0.23511700
H	-1.04249600	-2.82078100	-0.01920200
H	1.32546000	-3.48890600	0.07377000
C	3.44684300	-1.82230300	0.18681800
C	2.77040800	0.91345500	0.01294300
C	4.13711800	0.49249100	0.14264200
C	4.45672000	-0.83891500	0.22713500
H	4.91218200	1.25398300	0.16405500
H	5.49560400	-1.14475500	0.32008100
C	2.43583100	2.27058100	-0.09482800
C	1.11344600	2.65635000	-0.24877700
H	3.22541000	3.01736100	-0.06059500
H	0.83706500	3.69795300	-0.38236200
C	0.05500600	1.70424300	-0.33043900
O	-1.11215800	2.10572500	-0.65246700
C	-2.10644400	-0.41283000	0.01199000
C	-3.02372200	-1.11685000	-0.78574700
C	-2.61146100	0.49976200	0.95827300
C	-4.39185200	-0.90299500	-0.65905000
H	-2.65155200	-1.81115800	-1.53491400
C	-3.98053400	0.70208000	1.09248800
H	-1.92332200	1.02836400	1.61032500
C	-4.87676400	0.00654200	0.28255300
H	-5.08303300	-1.44269700	-1.30167000
H	-4.34855900	1.40704700	1.83343800
H	-5.94652100	0.17111000	0.38256100

E(UB3PW91/6-31G(d)): -806.113708
E(UB3PW91/6-31G(d) + ZPE): -805.865524
E(UB3PW91/cc-pVTZ//UB3PW91/6-31G(d)): -806.691048
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the transition state connecting **^{3}1a*** and **^{3}3a***.

C	-3.58477500	-1.69032700	0.00003700
C	-2.19141600	-1.42658800	0.00001600
C	-1.16998400	-2.42210200	-0.00003700
C	-4.49996600	-0.63529700	0.00005200
C	-1.78779900	-0.05789200	0.00002400
C	-2.71400700	1.02849800	0.00001600
C	-4.09176900	0.70111700	0.00003700
C	-2.18143500	2.35182500	-0.00003000
H	-2.87713300	3.18755800	-0.00003700
C	-0.80912600	2.62115000	-0.00007200
C	0.09554500	1.54709200	-0.00005500
C	-0.41652300	0.23024200	0.00001900
C	0.58030000	-0.75369800	-0.00002000
C	0.19069200	-2.09665600	-0.00007100

H	0.93329300	-2.89050500	-0.00011900
H	-5.56356300	-0.86076800	0.00006600
H	-4.83320800	1.49625100	0.00003500
H	-0.44383100	3.64297900	-0.00011500
H	-1.46439500	-3.46847300	-0.00006200
H	-3.93693200	-2.71872900	0.00003400
O	1.42682000	1.61209200	-0.00008200
C	1.96133400	-0.15634500	-0.00001500
C	2.73187300	-0.21781400	1.23647200
C	2.73194100	-0.21792600	-1.23644600
C	4.10647800	-0.18170100	1.22280200
H	2.18025300	-0.25782300	2.17034800
C	4.10655400	-0.18179300	-1.22269700
H	2.18037700	-0.25803800	-2.17035200
C	4.80873300	-0.15133600	0.00007100
H	4.65804100	-0.19400100	2.15885100
H	4.65817200	-0.19417900	-2.15871200
H	5.89447600	-0.12369300	0.00010200

E(UB3LYP/6-31G(d)): -806.405456
E(UB3LYP/6-31G(d) + ZPE): -806.158366
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.673618
One vibrational mode with imaginary frequency.

Optimized geometry (UB3PW91/6-31G*) for the transition state connecting ^{3}**1a*** and ^{3}**3a***.

C	-3.58542500	-1.67657000	0.00000700
C	-2.19323300	-1.41899200	0.00000800
C	-1.18035200	-2.41917200	0.00002400
C	-4.49488400	-0.61938600	-0.00001000
C	-1.78304000	-0.05496000	-0.00000700
C	-2.70346100	1.03263000	-0.00002400
C	-4.08072700	0.71282000	-0.00002500
C	-2.16713900	2.35136900	-0.00003900
H	-2.85965100	3.19026600	-0.00005300
C	-0.79699200	2.61555300	-0.00003800
C	0.10578300	1.54058500	-0.00002100
C	-0.41169100	0.22635500	-0.00000500
C	0.57743300	-0.76360100	0.00001000
C	0.17964200	-2.10229200	0.00002500
H	0.91828500	-2.90025000	0.00003700
H	-5.55979300	-0.84010500	-0.00001000
H	-4.81833900	1.51196600	-0.00003700
H	-0.42805000	3.63645400	-0.00005000
H	-1.48121700	-3.46416600	0.00003500
H	-3.94190300	-2.70383700	0.00001800
O	1.42853700	1.61170700	-0.00001800
C	1.96171900	-0.19159500	0.00001000
C	2.72446200	-0.23775400	1.23256000
C	2.72447600	-0.23779100	-1.23253000
C	4.09795200	-0.17374600	1.22042000
H	2.17229500	-0.28911800	2.16603300
C	4.09796700	-0.17378200	-1.22037600
H	2.17232000	-0.28918300	-2.16600700
C	4.79698700	-0.12920300	0.00002600
H	4.64924300	-0.17436600	2.15698600
H	4.64926900	-0.17443000	-2.15693400
H	5.88238200	-0.07969900	0.00003200

E(UB3PW91/6-31G(d)): -806.0998913
E(UB3PW91/6-31G(d) + ZPE): -805.852069
E(UB3PW91/cc-pVTZ//UB3PW91/6-31G(d)): -806.3519993
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the transition state connecting ^{3}**1a*** and ^{3}**4a***.

C	3.62553200	-1.59503200	0.11907400
C	2.22643400	-1.38458900	0.10093200
C	1.29607300	-2.45852700	0.15219400
C	4.50880000	-0.52128500	0.04326800
C	1.72551800	-0.04443500	0.01216200
C	2.64477200	1.04938700	-0.08579200
C	4.03261700	0.78382100	-0.06135700
C	2.11958100	2.36552600	-0.20908400
H	2.81241900	3.20063900	-0.27860900
C	0.75928100	2.59977100	-0.23490200
C	-0.16717500	1.53405700	-0.16354500
C	0.31828800	0.18832700	-0.00552900
C	-0.58413300	-0.91760100	0.07379700
C	-0.06712600	-2.22373200	0.12981000
H	-0.75792900	-3.05996200	0.20091700
H	5.58017600	-0.70344500	0.05883800
H	4.72847100	1.61624300	-0.13039700
H	0.36317100	3.60558200	-0.33277900
H	1.67261400	-3.47591700	0.21897000
H	4.00277100	-2.61215100	0.18800200
O	-1.45867900	1.81475100	-0.26661700
C	-2.02016900	-0.64341900	0.09280900
C	-2.96365800	-1.40172900	-0.60092500
C	-2.45424200	0.55202700	0.78026500
C	-4.30498300	-1.01149000	-0.63706100
H	-2.64046700	-2.27673800	-1.15741800
C	-3.83436000	0.91737800	0.74202900
H	-1.88243000	0.86593000	1.64825900
C	-4.73552000	0.15965200	0.02423700
H	-5.02147100	-1.60642900	-1.19664800
H	-4.15763900	1.79605700	1.29186600
H	-5.78342400	0.44352500	-0.01236300

E(UB3LYP/6-31G(d)): -806.415127
E(UB3LYP/6-31G(d) + ZPE): -806.166780
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.682804
One vibrational mode with imaginary frequency.

Optimized geometry (UB3PW91/6-31G*) for the transition state connecting ^{3}**1a*** and ^{3}**4a***.

C	3.61593300	-1.59499300	0.12573100
C	2.21962200	-1.38245800	0.10301500
C	1.28961400	-2.45393700	0.14985700
C	4.50026500	-0.52403400	0.05264400
C	1.72214700	-0.04422900	0.01260800
C	2.64121000	1.04577900	-0.08407400
C	4.02689900	0.77945500	-0.05472600
C	2.11899600	2.35980000	-0.21176400
H	2.81273000	3.19475800	-0.28025300
C	0.76095100	2.59583600	-0.24265800

C	-0.16665100	1.53261400	-0.17144200
C	0.31819100	0.18971500	-0.00958500
C	-0.58420800	-0.91227100	0.06718100
C	-0.07154300	-2.21760000	0.12262600
H	-0.76491300	-3.05250800	0.19198500
H	5.57157300	-0.70799600	0.07193800
H	4.72412300	1.61128900	-0.12270300
H	0.36676300	3.60236400	-0.34498300
H	1.66465400	-3.47224000	0.21761500
H	3.99156000	-2.61303100	0.19571700
O	-1.45099600	1.81354700	-0.27972800
C	-2.01675000	-0.63666900	0.08826000
C	-2.95678200	-1.38327900	-0.62185700
C	-2.45355700	0.53569800	0.79860400
C	-4.29576400	-0.99630500	-0.64795900
H	-2.62974900	-2.24464700	-1.19798300
C	-3.82787700	0.89908500	0.77192900
H	-1.86179300	0.86336000	1.64844600
C	-4.72816900	0.15582400	0.03927500
H	-5.01157000	-1.58001800	-1.22088200
H	-4.15353400	1.76392600	1.34256500
H	-5.77703100	0.43817800	0.01037700

E(UB3PW91/6-31G(d)): -806.1084454
E(UB3PW91/6-31G(d) + ZPE): -805.859444
E(UB3PW91/cc-pVTZ//UB3PW91/6-31G(d)): -806.360117
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for triplet biradical ^{3}**3a***.

C	-0.32717200	-2.00368200	-0.00003200
C	1.01716300	-2.40578100	-0.00001300
C	2.10330600	-1.47650100	0.00000600
C	1.78392200	-0.08839500	0.00000300
C	0.43550100	0.26473800	0.00000200
C	-0.62469700	-0.63939200	-0.00001900
H	3.78880800	-2.85127600	0.00003100
H	-1.11318400	-2.75417900	-0.00004900
H	1.24748700	-3.46827300	-0.00001700
C	3.48240900	-1.80839800	0.00002600
C	2.75050500	0.96026200	0.00000300
C	4.11107500	0.56266800	0.00002500
C	4.44634000	-0.79529000	0.00003800
H	4.89551700	1.31525100	0.00002600
H	5.49727100	-1.07388800	0.00005200
C	2.26788200	2.30439900	-0.00003100
C	0.90035400	2.63363100	-0.00002300
H	2.99513600	3.11238600	-0.00007400
H	0.58043800	3.67044900	-0.00004900
C	-0.02176200	1.58839700	0.00002200
O	-1.38166300	1.62865700	-0.00010900
C	-1.91616000	0.18723700	-0.00003000
C	-2.72370100	0.02206200	1.25189800
C	-2.72376300	0.02194600	-1.25190400
C	-4.05843100	-0.27082300	1.22586100
H	-2.18905600	0.14656900	2.18875400
C	-4.05849300	-0.27093600	-1.22577300
H	-2.18916500	0.14636600	-2.18879700
C	-4.75221200	-0.42724700	0.00006800
H	-4.59956600	-0.38450700	2.16193800

H	-4.59967300	-0.38470500	-2.16181300
H	-5.81309800	-0.65681900	0.00010600

E(UB3LYP/6-31G(d)): -806.409747
E(UB3LYP/6-31G(d) + ZPE): -806.161769
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.677466
No vibrational mode with imaginary frequency.

Optimized geometry (UB3PW91/6-31G*) for triplet biradical ^{3}**3a***.

C	-0.34203800	-1.99158100	0.00003100
C	0.99835600	-2.39947900	0.00003400
C	2.08828300	-1.47825700	0.00001600
C	1.77817200	-0.09109300	-0.00000500
C	0.43399300	0.26800700	-0.00000600
C	-0.63049400	-0.62732500	0.00001100
H	3.76546900	-2.86137100	0.00003100
H	-1.13237200	-2.73792300	0.00004400
H	1.22260500	-3.46367300	0.00004900
C	3.46341700	-1.81688000	0.00001600
C	2.74660100	0.95162100	-0.00002500
C	4.10331500	0.54831300	-0.00002400
C	4.43072200	-0.80949300	-0.00000400
H	4.89219400	1.29671100	-0.00003900
H	5.48054100	-1.09352500	-0.00000400
C	2.26990300	2.29518000	-0.00004500
C	0.90595600	2.63100100	-0.00004600
H	3.00050300	3.10064200	-0.00006100
H	0.59174500	3.66994700	-0.00006200
C	-0.01877200	1.59068300	-0.00002700
O	-1.37381000	1.63343300	-0.00002500
C	-1.90869800	0.21286000	0.00000100
C	-2.71408400	0.04326100	1.24966900
C	-2.71409900	0.04321800	-1.24965100
C	-4.04069400	-0.27868800	1.22394300
H	-2.18208500	0.18385300	2.18626000
C	-4.04070900	-0.27873000	-1.22389700
H	-2.18211200	0.18377800	-2.18625300
C	-4.72932900	-0.45288600	0.00003000
H	-4.57973300	-0.39946000	2.16067700
H	-4.57975900	-0.39953600	-2.16062000
H	-5.78531800	-0.70530500	0.00004100

E(UB3PW91/6-31G(d)): -806.106555
E(UB3PW91/6-31G(d) + ZPE): -805.857753
E(UB3PW91/cc-pVTZ//UB3PW91/6-31G(d)): -806.358516
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the first triplet excited state of **4a**, ^{3}**4a***.

C	3.66428000	-1.55715500	0.06979700
C	2.25600300	-1.37556900	0.07421600
C	1.34569900	-2.46124300	0.13114300
C	4.52047000	-0.46441800	-0.00485700
C	1.73134900	-0.04572700	0.01135000
C	2.62077300	1.07195000	-0.08153800
C	4.01590500	0.83433600	-0.08366700
C	2.06286600	2.37514200	-0.17774100

H	2.73165900	3.22841200	-0.25431200
C	0.68958300	2.57523400	-0.16960200
C	-0.18151300	1.48737300	-0.07337500
C	0.31986400	0.15531400	0.02085000
C	-0.56785500	-0.96001700	0.06376200
C	-0.02710900	-2.25240100	0.12084000
H	-0.69600400	-3.10631200	0.18294300
H	5.59571400	-0.62276700	-0.00792500
H	4.69422000	1.68116400	-0.15036000
H	0.26512800	3.57208200	-0.23661300
H	1.73880300	-3.47313400	0.18701900
H	4.06385600	-2.56666300	0.12111700
O	-1.51896900	1.73640800	-0.09139100
C	-2.00249500	-0.66698600	0.04400300
C	-2.99006200	-1.52020800	-0.37984400
C	-2.35231000	0.71012200	0.54662000
C	-4.35267700	-1.12628800	-0.41032100
H	-2.72462400	-2.51196500	-0.73733400
C	-3.78441800	1.09174900	0.38272100
H	-2.08197600	0.76785200	1.61918000
C	-4.72038300	0.19005500	-0.04629900
H	-5.10684700	-1.82694900	-0.75430600
H	-4.05347300	2.10871400	0.65256300
H	-5.76252100	0.49071500	-0.11918500

E(UB3LYP/6-31G(d)): -806.428841
E(UB3LYP/6-31G(d) + ZPE): -806.179482
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.695508
No vibrational mode with imaginary frequency.

Optimized geometry (UB3PW91/6-31G*) for the first triplet excited state of **4a**, ^{3}**4a***.

C	3.65773700	-1.55302700	0.07266600
C	2.25165200	-1.37221600	0.07547600
C	1.34407200	-2.45726900	0.13193300
C	4.51221800	-0.46124300	-0.00189500
C	1.72734200	-0.04547100	0.01153800
C	2.61383900	1.07049700	-0.08181400
C	4.00718800	0.83505100	-0.08254800
C	2.05588200	2.37089200	-0.18056200
H	2.72391100	3.22510400	-0.25850400
C	0.68437000	2.56977500	-0.17285600
C	-0.18450200	1.48265800	-0.07392900
C	0.31846000	0.15383200	0.02009000
C	-0.56666200	-0.95971500	0.05995800
C	-0.02716000	-2.24998000	0.11885300
H	-0.69614200	-3.10443300	0.18086800
H	5.58786600	-0.61891500	-0.00376600
H	4.68498800	1.68270900	-0.14977800
H	0.25923700	3.56666600	-0.24134500
H	1.73811400	-3.46910300	0.18957100
H	4.05811600	-2.56255800	0.12508500
O	-1.51670000	1.72975700	-0.08944300
C	-1.99780500	-0.66522600	0.03832300
C	-2.98487000	-1.51590200	-0.38561500
C	-2.34189600	0.70737700	0.54360600
C	-4.34555200	-1.12172500	-0.40942400
H	-2.72011700	-2.50667000	-0.74766600
C	-3.77130200	1.08937400	0.38851600

H	-2.06961800	0.75690000	1.61707700
C	-4.70974400	0.19106400	-0.03878500
H	-5.10186600	-1.82042600	-0.75365900
H	-4.03864600	2.10612200	0.66237300
H	-5.75185300	0.49407500	-0.10590700

E(UB3PW91/6-31G(d)): -806.124992
E(UB3PW91/6-31G(d) + ZPE): -805.874928
E(UB3PW91/cc-pVTZ//UB3PW91/6-31G(d)): -806.376106
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for **4a**.

C	3.60931500	-1.59033100	0.05867900
C	2.23148500	-1.38440800	0.03793100
C	1.28121700	-2.47349200	-0.02652600
C	4.50394200	-0.50400000	0.06136600
C	1.72548300	-0.04781100	0.03645500
C	2.63370800	1.05212100	-0.01319900
C	4.02836800	0.79246400	0.01581100
C	2.10038000	2.36476300	-0.12970300
H	2.78477300	3.20815500	-0.17665300
C	0.74143100	2.57961800	-0.18797800
C	-0.15056000	1.49205700	-0.07519000
C	0.31944000	0.17832800	0.04064100
C	-0.62121300	-0.93461000	0.01115700
C	-0.05946300	-2.26275500	-0.07284900
H	-0.72990300	-3.11477300	-0.11941400
H	5.57404000	-0.69053200	0.08101100
H	4.71933400	1.63166500	-0.00960900
H	0.32627700	3.57709300	-0.29111700
H	1.67171600	-3.48835300	-0.04695300
H	3.99441300	-2.60730100	0.06101200
O	-1.47955400	1.76573300	-0.14851900
C	-1.97331500	-0.64517800	0.07812200
C	-3.04095500	-1.57761600	-0.11907900
C	-2.33445200	0.77840800	0.48109100
C	-4.34285700	-1.17439100	-0.16662100
H	-2.80159400	-2.62218500	-0.29575600
C	-3.75014200	1.16585900	0.17253400
H	-2.15137000	0.88229400	1.57212000
C	-4.68763100	0.23175600	-0.07245100
H	-5.13116600	-1.89842300	-0.35029300
H	-3.98351900	2.22563200	0.21716100
H	-5.72165300	0.52617200	-0.23450500

E(B3LYP/6-31G(d)): -806.454169
E(B3LYP/6-31G(d) + ZPE): -806.202291
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.722191
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.727263 (pcm in benzene)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.735240 (pcm in acetonitrile)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.735776 (pcm in water)
No vibrational mode with imaginary frequency.

Optimized geometry (B3PW91/6-31G*) for **4a**.

C	3.60377200	-1.58535500	0.06423100
C	2.22737800	-1.38097000	0.03994000
C	1.28105600	-2.46907600	-0.02897100

C	4.49561900	-0.49992700	0.06951200
C	1.72126200	-0.04756400	0.03772100
C	2.62638900	1.05113200	-0.01146900
C	4.01899100	0.79435900	0.02146100
C	2.09267900	2.36056200	-0.13333600
H	2.77594400	3.20530300	-0.18109600
C	0.73542200	2.57324900	-0.19666800
C	-0.15419600	1.48677400	-0.08022800
C	0.31773800	0.17584800	0.03965300
C	-0.61897700	-0.93494400	0.00521300
C	-0.05857600	-2.25964800	-0.07999600
H	-0.72811900	-3.11280200	-0.13017400
H	5.56624400	-0.68494100	0.09218200
H	4.70931000	1.63457400	-0.00340600
H	0.31959600	3.57037000	-0.30481100
H	1.67225200	-3.48405500	-0.04922500
H	3.98991400	-2.60234000	0.06704200
O	-1.47807200	1.75748900	-0.15435100
C	-1.96953600	-0.64414900	0.07170400
C	-3.03526400	-1.57323000	-0.12647600
C	-2.32319900	0.77468400	0.47873600
C	-4.33624700	-1.16956200	-0.16284300
H	-2.79748400	-2.61696100	-0.31270900
C	-3.73731500	1.16373000	0.18462500
H	-2.13114900	0.87380400	1.56928500
C	-4.67766000	0.23312800	-0.05771200
H	-5.12597700	-1.89235000	-0.34729500
H	-3.96974300	2.22384700	0.23517200
H	-5.71221900	0.53140000	-0.21073400

E(B3PW91/6-31G(d)): -806.1490578
E(B3PW91/6-31G(d) + ZPE): -805.896471
E(B3PW91/cc-pVTZ//B3PW91/6-31G(d)): -806.401331
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for the transition state connecting **4a** and **1a**.

C	3.60998800	-1.57981300	0.12864900
C	2.22233800	-1.36962000	0.13364900
C	1.28559400	-2.45616300	0.11396200
C	4.49900600	-0.50783700	0.03257800
C	1.71148400	-0.03734000	0.08544800
C	2.62536200	1.04307100	-0.09715400
C	4.00944900	0.78772500	-0.10192500
C	2.08951000	2.34369100	-0.35759800
H	2.78054300	3.16557600	-0.53168700
C	0.74248800	2.56375100	-0.41068400
C	-0.18671200	1.53403300	-0.04145100
C	0.30396800	0.19544500	0.15930500
C	-0.60867300	-0.91618700	0.13965200
C	-0.05969700	-2.23811900	0.05483500
H	-0.74328000	-3.08112600	0.03446200
H	5.56989900	-0.68851900	0.02882500
H	4.69703200	1.61989700	-0.23383900
H	0.33209100	3.54585500	-0.62146000
H	1.67281000	-3.47243600	0.12997200
H	3.98838400	-2.59811900	0.17792800
O	-1.42923000	1.88362000	0.08998800
C	-2.00305600	-0.65946900	0.13973400

C	-2.95260800	-1.47124000	-0.53699900
C	-2.42872800	0.59467600	0.75824100
C	-4.26136300	-1.07666300	-0.67144800
H	-2.61272900	-2.38784100	-1.01221400
C	-3.81887100	0.97348800	0.57953200
H	-2.00793000	0.77903300	1.74921300
C	-4.67865500	0.17057000	-0.11346700
H	-4.96986300	-1.68751600	-1.22197900
H	-4.16017200	1.89879900	1.03397400
H	-5.71789100	0.47344300	-0.22226600

E(B3LYP/6-31G(d)): -806.441450
E(B3LYP/6-31G(d) + ZPE): -806.191115
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.709497
One vibrational mode with imaginary frequency.

Optimized geometry (B3PW91/6-31G*) for the transition state connecting **4a** and **1a**.

C	3.60530500	-1.57276400	0.13613000
C	2.21858200	-1.36514800	0.13754500
C	1.28679900	-2.45148200	0.11408500
C	4.49059600	-0.50127800	0.04014300
C	1.70656900	-0.03654500	0.08743600
C	2.61662000	1.04274700	-0.09792700
C	3.99852300	0.79142200	-0.10009200
C	2.07910700	2.33853800	-0.36845100
H	2.76862000	3.16103000	-0.54814800
C	0.73374100	2.55475000	-0.42672800
C	-0.19273000	1.52950600	-0.04288800
C	0.30177200	0.19300000	0.16130900
C	-0.60514900	-0.91683700	0.13671200
C	-0.05766700	-2.23519000	0.04941500
H	-0.74144400	-3.07873500	0.02542800
H	5.56225300	-0.67934100	0.03889200
H	4.68479100	1.62464500	-0.23539600
H	0.32147500	3.53455100	-0.64662200
H	1.67533500	-3.46762500	0.13148600
H	3.98547100	-2.59071000	0.18766400
O	-1.42679700	1.87918300	0.09786400
C	-1.99912500	-0.65945400	0.13570800
C	-2.94172800	-1.45764800	-0.55873400
C	-2.42106000	0.58134700	0.76904600
C	-4.25013300	-1.06240600	-0.68727800
H	-2.59872800	-2.36452600	-1.05137700
C	-3.80881600	0.95709200	0.60639600
H	-1.98533600	0.76253200	1.75464300
C	-4.66772900	0.16797200	-0.10313900
H	-4.95710100	-1.66303100	-1.25150200
H	-4.15380000	1.87048400	1.08242800
H	-5.70802700	0.47153000	-0.20253600

E(B3PW91/6-31G(d)): -806.135029
E(B3PW91/6-31G(d) + ZPE): -805.884013
E(B3PW91/cc-pVTZ//B3PW91/6-31G(d)): -806.387056
One vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for the transition state of hydrogen abstraction from **4a** by TCNE.

C	-4.96811800	0.62743300	0.75083300
C	-3.63800200	0.96858300	0.47755400
C	-3.08169400	2.24813900	0.81965100
C	-5.47758100	-0.62323000	0.38061100
C	-2.79851300	0.02126000	-0.17888300
C	-3.32359700	-1.24377200	-0.57273200
C	-4.67219500	-1.54394200	-0.27464300
C	-2.47086400	-2.15259500	-1.26245700
H	-2.86338100	-3.12147700	-1.55724600
C	-1.16339400	-1.83558400	-1.54364800
C	-0.64677400	-0.59170400	-1.12432000
C	-1.44134200	0.35169100	-0.44970400
C	-0.90736400	1.64221300	-0.10121100
C	-1.78832400	2.57666500	0.53290000
H	-1.41524800	3.55499900	0.81338600
H	-6.51090000	-0.87061100	0.60428900
H	-5.07322000	-2.51068200	-0.56723200
H	-0.50285400	-2.52988100	-2.04877400
H	-3.72184800	2.96909100	1.32160000
H	-5.60828900	1.34703300	1.25447200
O	0.64425200	-0.33443500	-1.43750000
C	0.43633800	1.91321400	-0.42870600
C	1.08611600	3.16989300	-0.27329400
C	1.27676300	0.80401500	-0.90087600
C	2.35029300	3.38575400	-0.76425600
H	0.55153700	3.99050600	0.19274400
C	2.50476300	1.12257300	-1.61966900
H	1.77147200	0.28733600	0.20918100
C	3.04763200	2.36361000	-1.48298600
H	2.81177700	4.36159100	-0.65064300
H	2.99837700	0.32141500	-2.15997000
H	4.00567600	2.59107900	-1.93996500
C	2.36651300	-0.65818300	1.21245000
C	2.57597200	-1.91358600	0.54357700
C	3.73531800	-2.12300600	-0.24134100
N	4.67981200	-2.28892900	-0.90844600
C	1.56185900	-2.89662100	0.51684900
N	0.71217200	-3.69765900	0.47515200
C	1.31283500	-0.55834900	2.19921200
N	0.44480400	-0.41809000	2.95956700
C	3.52896600	0.15343300	1.50832900
N	4.44453400	0.83862800	1.71497100

E(B3LYP/6-31G(d)): -1253.968275
E(B3LYP/6-31G(d) + ZPE): -1253.672812
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -1254.387347
One vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for the transition state of hydrogen abstraction from **4a** by *p*-benzoquinone.

C	5.14482000	-0.86053400	-0.89916200
C	4.01504000	-0.07622500	-0.64945100
C	3.92057700	1.30094500	-1.06058200
C	5.20704300	-2.19433100	-0.46521500
C	2.91115200	-0.65067800	0.05284200
C	2.98463600	-2.00069900	0.51041400

C	4.15060200	-2.75665900	0.22978100
C	1.88806000	-2.52964300	1.24412200
H	1.93698700	-3.55627300	1.59708700
C	0.77276400	-1.76528200	1.51127700
C	0.69788000	-0.44398800	1.03154500
C	1.74971600	0.13442000	0.30560700
C	1.67769700	1.51388300	-0.12476500
C	2.81525300	2.05776200	-0.80242400
H	2.79187800	3.08961100	-1.13647000
H	6.09483200	-2.78477000	-0.67288900
H	4.20445500	-3.78666400	0.57290100
H	-0.06801200	-2.15827500	2.07324100
H	4.76342500	1.73653900	-1.59110800
H	5.98504800	-0.42530500	-1.43424200
O	-0.42252100	0.25616200	1.35071100
C	0.49427900	2.22059300	0.14806500
C	0.26707300	3.59934100	-0.13680200
C	-0.65824500	1.47730900	0.66803600
C	-0.88968300	4.22936300	0.24963700
H	1.04575300	4.17629500	-0.62450400
C	-1.76000900	2.21196800	1.25946900
H	-1.23111400	1.04745000	-0.45496500
C	-1.90570100	3.53885800	0.98482800
H	-1.01870600	5.28654200	0.03603100
H	-2.48878100	1.65259000	1.83739100
H	-2.77157000	4.08523500	1.34637600
O	-1.74561200	0.37872900	-1.37771300
C	-2.75853400	-0.34880000	-1.02285300
C	-2.58737600	-1.74491000	-0.70333200
C	-3.65009700	-2.52211700	-0.36242200
H	-1.57873300	-2.14568200	-0.76228900
H	-3.54077900	-3.57856200	-0.13399100
C	-4.08239100	0.21887000	-0.93949000
C	-5.15398600	-0.54485600	-0.59354900
H	-4.18454900	1.27372000	-1.18241400
H	-6.15929900	-0.13650000	-0.54135500
C	-5.01231400	-1.97421700	-0.27807600
O	-5.98316400	-2.67466700	0.04277500

E(B3LYP/6-31G(d)): -1187.889202
E(B3LYP/6-31G(d) + ZPE): -1187.556062
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -1188.297195
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) of radical **5a**.

C	3.14966000	2.39267800	0.00000000
C	2.29203400	1.27012300	0.00000000
C	2.77221700	-0.07051300	0.00000000
C	2.62797100	3.68710400	0.00000000
C	0.87802400	1.48371400	0.00000000
C	0.34926500	2.81288400	0.00000000
C	1.25438700	3.90411700	0.00000000
C	-1.06100800	2.98302300	0.00000000
H	-1.47007500	3.98965200	0.00000000
C	-1.91629200	1.89265100	0.00000000
C	-1.39028900	0.59880400	0.00000000
C	0.00000000	0.35939500	0.00000000
C	0.51184800	-0.97320200	0.00000000
C	1.90712500	-1.15052500	0.00000000

H	2.32339800	-2.15294300	0.00000000
H	3.30523900	4.53720500	0.00000000
H	0.85869000	4.91649700	0.00000000
H	-2.99440000	2.01742800	0.00000000
H	3.84599100	-0.23921100	0.00000000
H	4.22513600	2.23543700	0.00000000
O	-2.28794700	-0.43821200	0.00000000
C	-0.46406000	-2.05933400	0.00000000
C	-0.13235600	-3.42852500	0.00000000
C	-1.83820600	-1.73688300	0.00000000
C	-1.11097400	-4.41576600	0.00000000
H	0.91262900	-3.72099400	0.00000000
C	-2.82839500	-2.71819600	0.00000000
C	-2.46447200	-4.06152700	0.00000000
H	-0.82024000	-5.46223800	0.00000000
H	-3.86805200	-2.40693100	0.00000000
H	-3.23361900	-4.82834300	0.00000000

E(UB3LYP/6-31G(d)): -805.895187
E(UB3LYP/6-31G(d) + ZPE): -805.655126
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.160459
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.165076 (pcm in benzene)
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.172334 (pcm in acetonitrile)
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -806.172843 (pcm in water)
No vibrational mode with imaginary frequency.

Optimized geometry (UB3PW91/6-31G*) of radical **5a**.

C	3.13367500	2.40210600	0.00000000
C	2.28240100	1.27732700	0.00000000
C	2.76894600	-0.05835800	0.00000000
C	2.60655200	3.69220800	0.00000000
C	0.87030200	1.48397400	0.00000000
C	0.33611900	2.80769900	0.00000000
C	1.23380000	3.90209500	0.00000000
C	-1.07226800	2.97143400	0.00000000
H	-1.48619000	3.97645700	0.00000000
C	-1.92112400	1.87847900	0.00000000
C	-1.38931900	0.58904600	0.00000000
C	0.00000000	0.35733900	0.00000000
C	0.51693900	-0.97016500	0.00000000
C	1.91050900	-1.14153800	0.00000000
H	2.33193600	-2.14223900	0.00000000
H	3.27996800	4.54578200	0.00000000
H	0.83286000	4.91279500	0.00000000
H	-3.00019700	1.99808800	0.00000000
H	3.84390700	-0.22158100	0.00000000
H	4.21029900	2.25018600	0.00000000
O	-2.27958600	-0.44702300	0.00000000
C	-0.45356300	-2.05682100	0.00000000
C	-0.11892000	-3.42269700	0.00000000
C	-1.82614700	-1.73858300	0.00000000
C	-1.09310700	-4.41161800	0.00000000
H	0.92723000	-3.71294300	0.00000000
C	-2.81235400	-2.72155000	0.00000000
C	-2.44543800	-4.06185400	0.00000000
H	-0.79911600	-5.45751000	0.00000000
H	-3.85324700	-2.41306900	0.00000000
H	-3.21277700	-4.83092300	0.00000000

E(UB3PW91/6-31G(d)): -805.590121
E(UB3PW91/6-31G(d) + ZPE): -805.349343
E(UB3PW91/cc-pVTZ//UB3PW91/6-31G(d)): -805.840107
No vibrational mode with imaginary frequency.

Optimized geometry (UM05-2X/6-31G*) of radical **5a**.

C	3.13710200	2.38255800	0.00000000
C	2.28076800	1.26551400	0.00000000
C	2.76334300	-0.07051100	0.00000000
C	2.61715300	3.67366400	0.00000000
C	0.87385600	1.47860300	0.00000000
C	0.34787500	2.80024800	0.00000000
C	1.24759200	3.88946800	0.00000000
C	-1.05836400	2.97237400	0.00000000
H	-1.46327600	3.97626900	0.00000000
C	-1.91052900	1.88567700	0.00000000
C	-1.38544700	0.59538200	0.00000000
C	0.00000000	0.35767900	0.00000000
C	0.51176300	-0.96696900	0.00000000
C	1.90132500	-1.14762900	0.00000000
H	2.31525400	-2.14656100	0.00000000
H	3.29163800	4.52049600	0.00000000
H	0.85084100	4.89699100	0.00000000
H	-2.98519600	2.00635200	0.00000000
H	3.83340400	-0.23530000	0.00000000
H	4.20812100	2.22356300	0.00000000
O	-2.28044400	-0.43625700	0.00000000
C	-0.46402900	-2.05114600	0.00000000
C	-0.12999000	-3.41363100	0.00000000
C	-1.83017500	-1.73005000	0.00000000
C	-1.10396400	-4.39934100	0.00000000
H	0.91192900	-3.70325100	0.00000000
C	-2.81707300	-2.70842300	0.00000000
C	-2.45365700	-4.04687400	0.00000000
H	-0.81292700	-5.44149600	0.00000000
H	-3.85226600	-2.39501500	0.00000000
H	-3.21926300	-4.81154600	0.00000000

E(UM05-2X/6-31G(d)): -805.830012
E(UM05-2X/6-31G(d) + ZPE): -805.585705
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) of cation **6a**.

C	2.57882200	3.70928600	0.00000000
C	3.11196900	2.42211500	0.00000000
C	2.26724200	1.29287700	0.00000000
C	0.85898600	1.48669600	0.00000000
C	0.31459800	2.80139100	0.00000000
C	1.19613500	3.89980000	0.00000000
C	2.76540500	-0.04306100	0.00000000
C	0.00000000	0.35549400	0.00000000
C	0.51862800	-0.97001900	0.00000000
C	1.92749400	-1.13534300	0.00000000
C	-0.42938600	-2.05900900	0.00000000
C	-1.81034900	-1.74920500	0.00000000
C	-1.39684800	0.57501600	0.00000000
C	-1.95063900	1.87283500	0.00000000

C	-1.10583000	2.95711300	0.00000000
H	-1.52251300	3.96039300	0.00000000
H	-3.02929300	1.98281500	0.00000000
H	3.84128100	-0.19662200	0.00000000
H	3.24132700	4.56856900	0.00000000
H	4.18918000	2.28016400	0.00000000
H	0.78868800	4.90711900	0.00000000
H	2.35682900	-2.12995300	0.00000000
C	-0.07859500	-3.43026500	0.00000000
C	-1.05244300	-4.41050100	0.00000000
H	0.96634200	-3.71882300	0.00000000
H	-0.76438700	-5.45656800	0.00000000
C	-2.41708400	-4.06167300	0.00000000
C	-2.80232300	-2.73112900	0.00000000
H	-3.17434000	-4.83919200	0.00000000
H	-3.84434500	-2.43071600	0.00000000
O	-2.25293300	-0.45271100	0.00000000

E(B3LYP/6-31G(d)): -805.698162
E(B3LYP/6-31G(d) + ZPE): -805.454981
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -805.955253
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -805.993364 (pcm in benzene)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.025083 (pcm in acetonitrile)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -806.026615 (pcm in water)
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) of 1,1,2,2-tetracyanoethyl radical.

C	-0.76613600	0.02971200	0.01741400
C	0.58147600	-0.46231700	-0.53805200
H	0.37018500	-1.15625000	-1.36181400
C	1.37160700	0.65912800	-1.08198800
N	1.97450600	1.54353700	-1.52703300
C	1.33854900	-1.20002200	0.49210300
N	1.91405300	-1.79833400	1.30119500
C	-1.95119900	-0.46106200	-0.54058000
N	-2.92314800	-0.89276000	-1.03275800
C	-0.80502800	0.95328500	1.07066200
N	-0.82052400	1.72525700	1.95066100

E(UB3LYP/6-31G(d)): -448.095750
E(UB3LYP/6-31G(d) + ZPE): -448.038799
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -448.251580
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -448.260185 (pcm in benzene)
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -448.272836 (pcm in acetonitrile)
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -448.274246 (pcm in water)
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) of 1,1,2,2-tetracyanoethyl anion.

C	0.79260500	0.04916400	-0.00685800
C	-0.56253300	-0.56743400	0.29336000
H	-0.37104700	-1.52320200	0.79943400
C	-1.40012400	0.23067200	1.22770100
N	-2.02713000	0.85229100	1.98250900
C	-1.36385600	-0.89709800	-0.91606500
N	-1.95866900	-1.17873400	-1.87333700
C	1.93313500	-0.67986400	0.35289700

N	2.86755900	-1.31954600	0.66956900
C	0.87835500	1.29980900	-0.63598000
N	0.93331900	2.34766200	-1.16299400

E(B3LYP/6-31G(d)): -448.224120
E(B3LYP/6-31G(d) + ZPE): -448.166645
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -448.392371
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -448.436083 (pcm in benzene)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -448.472759 (pcm in acetonitrile)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -448.474318 (pcm in water)
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) of tetracyanoethene.

C	0.00000000	0.00000000	0.68622500
C	0.00000000	0.00000000	-0.68622500
C	0.00000000	1.21902000	-1.43314400
N	0.00000000	2.19978700	-2.05779700
C	0.00000000	1.21902000	1.43314400
N	0.00000000	2.19978700	2.05779700
C	0.00000000	-1.21902000	1.43314400
N	0.00000000	-2.19978700	2.05779700
C	0.00000000	-1.21902000	-1.43314400
N	0.00000000	-2.19978700	-2.05779700

E(B3LYP/6-31G(d)): -447.518338
E(B3LYP/6-31G(d) + ZPE): -447.471683
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -447.672934
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -447.679299 (pcm in benzene)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -447.689081 (pcm in acetonitrile)
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -447.689507 (pcm in water)
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) of 9-(4-methoxyphenyl)-phenalenone **1b**.

C	0.41184800	-2.00332800	0.07854700
C	1.71767800	-2.42860400	0.11040900
C	2.77996300	-1.49418200	0.08427200
C	2.46168600	-0.10500800	-0.00577700
C	1.09593000	0.32976400	-0.05388000
C	0.06401800	-0.62606900	0.01649300
H	4.35162200	-2.97500600	0.20895100
H	-0.39349400	-2.72930000	0.13432600
H	1.94761100	-3.48971200	0.17265200
C	4.13638400	-1.91152800	0.13993000
C	3.54454200	0.83261900	-0.05192600
C	4.85775800	0.38196900	0.00917100
C	5.15992900	-0.98992600	0.10620700
H	5.66543800	1.10948200	-0.02269800
H	6.19555500	-1.31404600	0.15037100
C	3.24886400	2.24479500	-0.17081500
C	1.98162800	2.69423400	-0.26984500
H	4.08753000	2.93835200	-0.19231300
H	1.74761400	3.74854800	-0.38051900
C	0.81944200	1.79121300	-0.25603900
O	-0.30940600	2.25227600	-0.42459600
C	-1.39547100	-0.33101700	0.06693500
C	-2.26502000	-0.95612000	-0.83237900

C	-1.96052300	0.46799300	1.07848200
C	-3.65024600	-0.77893700	-0.76149700
H	-1.85721500	-1.57824900	-1.62506000
C	-3.33076500	0.63463500	1.17738100
H	-1.31244400	0.95947000	1.79662700
C	-4.18917000	0.01847400	0.25139800
H	-4.28579000	-1.26523000	-1.49272900
H	-3.76731700	1.24575600	1.96109500
O	-5.52108200	0.25679400	0.43031000
C	-6.43378400	-0.32464100	-0.48603700
H	-7.42608000	0.00201600	-0.16936000
H	-6.24893200	0.01912000	-1.51240000
H	-6.38833400	-1.42177600	-0.46083100

E(B3LYP/6-31G(d)): -921.010436
E(B3LYP/6-31G(d) + ZPE): -920.726696
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -921.323328
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) of the first excited triplet state of 9-(4-methoxyphenyl)-phenalenone, **^{3}1b***.

C	0.57411100	-2.13579400	-0.05185400
C	1.91975000	-2.42596000	0.09390100
C	2.88781000	-1.38857300	0.17004600
C	2.44226000	-0.02807200	0.02892700
C	1.06482400	0.25639500	-0.16834700
C	0.09501700	-0.81715200	-0.13218900
H	4.58793300	-2.68237900	0.44905300
H	-0.14630900	-2.94874700	-0.03444300
H	2.24720300	-3.45768700	0.19113000
C	4.25710800	-1.65155800	0.35496100
C	3.41846100	1.03295900	0.05901100
C	4.79432000	0.70763900	0.26642200
C	5.19529000	-0.60333600	0.41039500
H	5.51977700	1.51595700	0.29849400
H	6.24625300	-0.83550000	0.56136300
C	2.99186200	2.36678100	-0.11432800
C	1.65986700	2.65845900	-0.34184600
H	3.72756400	3.16586400	-0.06790100
H	1.32342000	3.67463700	-0.52154300
C	0.67356400	1.63157400	-0.44501300
O	-0.51091200	1.93959200	-0.83496100
C	-1.35727600	-0.59059900	-0.12091500
C	-2.21902500	-1.41266100	-0.88267800
C	-1.95977500	0.37675900	0.71573000
C	-3.59231700	-1.25829300	-0.83571400
H	-1.79033800	-2.15521200	-1.54920400
C	-3.34143300	0.53142400	0.78365300
H	-1.33604700	0.98627400	1.35892900
C	-4.16849400	-0.27997100	-0.00133300
H	-4.25099900	-1.87145300	-1.44275200
H	-3.75837500	1.27994000	1.44721900
O	-5.52560100	-0.21326300	-0.02861800
C	-6.17082900	0.77283200	0.76586400
H	-7.23859900	0.66003500	0.57126500
H	-5.97745100	0.61614700	1.83487400
H	-5.85250700	1.78438200	0.48399300

E(UB3LYP/6-31G(d)): -920.947323

E(UB3LYP/6-31G(d) + ZPE): -920.666671
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -921.258994
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the transition state connecting ^{3}**1b*** and ^{3}**3b***.

C	-4.27888100	-1.71665500	-0.09554000
C	-2.88908100	-1.43864300	-0.04291200
C	-1.85597900	-2.42166500	-0.00179900
C	-5.20370300	-0.67036400	-0.13182500
C	-2.50155700	-0.06550100	-0.02964500
C	-3.43683600	1.01249500	-0.06563600
C	-4.81019900	0.67064700	-0.11790800
C	-2.91568600	2.34059800	-0.04525300
H	-3.61869600	3.16987200	-0.07212300
C	-1.54608000	2.62270200	0.00823700
C	-0.63287800	1.55700800	0.04334200
C	-1.13535800	0.23661500	0.02259900
C	-0.12724200	-0.73267600	0.06210600
C	-0.49960300	-2.08025900	0.04996900
H	0.25179600	-2.86538600	0.08034800
H	-6.26425200	-0.90680100	-0.17199600
H	-5.55990500	1.45755900	-0.14672400
H	-1.19170200	3.64842300	0.02331700
H	-2.13791000	-3.47161600	-0.01096400
H	-4.62103000	-2.74842900	-0.10713000
O	0.69740700	1.62000800	0.09762000
C	1.24143800	-0.10307200	0.11509500
C	1.97866300	-0.18832400	1.37572200
C	2.06508900	-0.17927800	-1.08752400
C	3.34346100	-0.16073400	1.41261100
H	1.40146400	-0.23716700	2.29334300
C	3.43929900	-0.14572000	-1.03854900
H	1.55332900	-0.22276800	-2.04350700
C	4.09922000	-0.11893300	0.21042000
H	3.88553300	-0.18751100	2.35296700
H	4.00691700	-0.16302900	-1.96228200
O	5.44095800	-0.08438800	0.37295300
C	6.27676200	-0.03417600	-0.77986500
H	6.06700900	0.85707700	-1.38293500
H	7.29866600	0.01300900	-0.40157300
H	6.15676400	-0.93257900	-1.39720000

E(UB3LYP/6-31G(d)): -920.933822
E(UB3LYP/6-31G(d) + ZPE): -920.653484
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -921.245723
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the transition state connecting ^{3}**1b*** and ^{3}**4b***.

C	4.35742900	-1.56784900	0.06613700
C	2.95529700	-1.37436600	0.08074900
C	2.03813800	-2.45717600	0.16323900
C	5.22477300	-0.48361500	-0.03733800
C	2.43745600	-0.04032200	-0.00447600
C	3.33980100	1.06479600	-0.13047800

C	4.73109900	0.81563800	-0.13781600
C	2.79419800	2.37321100	-0.24774800
H	3.47425200	3.21672600	-0.33905400
C	1.43005200	2.59025300	-0.24161600
C	0.52085600	1.51313900	-0.14286400
C	1.02832500	0.17586200	0.00980700
C	0.13947900	-0.93775500	0.11893700
C	0.67126300	-2.23715300	0.17447900
H	-0.00824300	-3.08022900	0.27080600
H	6.29844800	-0.65271100	-0.04636700
H	5.41549700	1.65555500	-0.22768600
H	1.01902100	3.59051700	-0.33519400
H	2.42704600	-3.47010000	0.22826600
H	4.74891000	-2.57974800	0.13264100
O	-0.77923400	1.77024200	-0.21374900
C	-1.29722700	-0.67171200	0.16770400
C	-2.25298000	-1.43105600	-0.50035800
C	-1.72837700	0.53357500	0.85228500
C	-3.60024800	-1.05597200	-0.51680500
H	-1.94290000	-2.30780600	-1.06150700
C	-3.10766900	0.87964900	0.85838400
H	-1.14683900	0.84675900	1.71439200
C	-4.02569200	0.11876500	0.15506200
H	-4.31052700	-1.66297600	-1.06589300
H	-3.45133100	1.74322100	1.41731600
O	-5.31966100	0.54153800	0.19237400
C	-6.31570300	-0.23188400	-0.46142600
H	-7.25843300	0.28738400	-0.28137700
H	-6.13771100	-0.29015900	-1.54296700
H	-6.37765300	-1.24683700	-0.04751900

E(UB3LYP/6-31G(d)): -920.937013
E(UB3LYP/6-31G(d) + ZPE): -920.656072
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -921.248153
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for triplet biradical ^{3}**3b***.

C	0.35156100	-1.98582800	0.07766500
C	1.68641500	-2.41572500	0.03454200
C	2.78928600	-1.50845300	-0.01869700
C	2.49672400	-0.11406600	-0.02801600
C	1.15617700	0.26674800	0.01587000
C	0.07933400	-0.61609400	0.06811900
H	4.44534400	-2.91787100	-0.05828600
H	-0.44888200	-2.72004900	0.11825400
H	1.89577300	-3.48258100	0.04231900
C	4.16063200	-1.86882100	-0.06313700
C	3.48475400	0.91343800	-0.07817200
C	4.83605900	0.48805700	-0.12095500
C	5.14425000	-0.87624400	-0.11267200
H	5.63463700	1.22468100	-0.15988000
H	6.18876500	-1.17640100	-0.14594600
C	3.03069100	2.26732500	-0.08038800
C	1.67173100	2.62502300	-0.03549200
H	3.77440400	3.05943500	-0.11819500
H	1.37383400	3.66847200	-0.03841400
C	0.72518900	1.60120000	0.01360700
O	-0.62800100	1.67532600	0.06373900
C	-1.20067300	0.21861600	0.10541400

C	-1.96740400	0.10566200	1.38308100
C	-2.06170300	0.07048200	-1.10485400
C	-3.32006500	-0.03262000	1.41387400
H	-1.39220200	0.15873300	2.30215900
C	-3.42474100	-0.06369200	-1.03869500
H	-1.55745500	0.09743700	-2.06572500
C	-4.08193300	-0.11106400	0.21303300
H	-3.85578600	-0.09548200	2.35673600
H	-3.99194000	-0.14472100	-1.95997200
O	-5.42192000	-0.24368700	0.38486300
C	-6.25648500	-0.31641400	-0.76437900
H	-6.02024900	-1.19669500	-1.37527800
H	-7.27634000	-0.40135600	-0.38612700
H	-6.16932400	0.58810500	-1.37894300

E(UB3LYP/6-31G(d)): -920.935589
E(UB3LYP/6-31G(d) + ZPE): -920.654567
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -921.246949
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the first triplet excited state of **4b**, ^{3}**4b***.

C	4.38748500	-1.54164400	0.01729000
C	2.97918300	-1.36989500	0.05177900
C	2.07706400	-2.46200500	0.13067900
C	5.23465400	-0.44278100	-0.07817000
C	2.44390200	-0.04385500	-0.00245900
C	3.32314200	1.07977600	-0.11719500
C	4.71974500	0.85183900	-0.14884600
C	2.75396300	2.37873100	-0.20499500
H	3.41490800	3.23654000	-0.29764400
C	1.37996300	2.56887200	-0.16963500
C	0.51871500	1.47479400	-0.05208900
C	1.03153500	0.14756600	0.03713700
C	0.15219000	-0.97383700	0.10401200
C	0.70352400	-2.26271200	0.15127000
H	0.04204100	-3.12108300	0.23098500
H	6.31065400	-0.59396100	-0.10407900
H	5.39043300	1.70328400	-0.23220200
H	0.94673000	3.56223400	-0.23212100
H	2.47846700	-3.47101800	0.18014500
H	4.79530500	-2.54820200	0.06212600
O	-0.82080000	1.71450300	-0.04850600
C	-1.28247500	-0.68884700	0.11650600
C	-2.27740500	-1.54232100	-0.27652700
C	-1.63462700	0.68726800	0.61512200
C	-3.64859700	-1.16536800	-0.28219000
H	-2.02257700	-2.53747600	-0.63205400
C	-3.06735900	1.05860800	0.48854100
H	-1.33677700	0.75327400	1.68039600
C	-4.02096400	0.14709800	0.08638100
H	-4.38927900	-1.88499200	-0.60768300
H	-3.36299500	2.06513400	0.76424200
O	-5.31126800	0.60127600	0.06757700
C	-6.33357800	-0.27379700	-0.38045800
H	-7.26041300	0.30041800	-0.32701100
H	-6.16804000	-0.59565800	-1.41721700
H	-6.42227100	-1.15966100	0.26261700

E(UB3LYP/6-31G(d)): -920.949204
E(UB3LYP/6-31G(d) + ZPE): -920.667357
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -921.259381
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for **4b**.

C	-4.32886100	1.57275700	0.00295600
C	-2.94894900	1.37747900	0.01858200
C	-2.00613000	2.47369300	-0.01715500
C	-5.21431300	0.47991600	-0.02607500
C	-2.43258800	0.04507300	0.02362800
C	-3.33021100	-1.06102100	-0.06171700
C	-4.72666100	-0.81270400	-0.06899000
C	-2.78245900	-2.36817300	-0.17919400
H	-3.45853400	-3.21632000	-0.25395800
C	-1.42125700	-2.57189500	-0.20502300
C	-0.53938700	-1.47952200	-0.05168800
C	-1.02575900	-0.17038600	0.06686700
C	-0.09442500	0.94928400	0.06661200
C	-0.66270200	2.27310300	-0.03066100
H	0.00248300	3.13029700	-0.05589400
H	-6.28602600	0.65763600	-0.03438900
H	-5.40995300	-1.65696800	-0.12102600
H	-0.99556000	-3.56473000	-0.30950100
H	-2.40353300	3.48576600	-0.04324900
H	-4.72172200	2.58677500	0.00075600
O	0.78994500	-1.74217400	-0.08890700
C	1.25791200	0.66617400	0.16721100
C	2.32211900	1.59815000	-0.02485000
C	1.61816300	-0.75114000	0.58579100
C	3.63017700	1.21214200	-0.03786500
H	2.08349400	2.63863800	-0.22522600
C	3.04204000	-1.12799500	0.33942800
H	1.36767200	-0.86375300	1.66220100
C	3.98758800	-0.19053700	0.10803300
H	4.40276300	1.95039900	-0.21562300
H	3.31486700	-2.17313500	0.43744600
O	5.28766200	-0.61664400	0.01313900
C	6.28571600	0.28438100	-0.43762900
H	7.20198700	-0.30508400	-0.51258800
H	6.04841900	0.70270400	-1.42469400
H	6.45270900	1.10562300	0.27232700

E(B3LYP/6-31G(d)): -920.973244
E(B3LYP/6-31G(d) + ZPE): -920.688929
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -921.284731
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for the transition state connecting **4b** and **1b**.

C	4.32597500	-1.56973100	0.06179000
C	2.93902500	-1.36651600	0.09919800
C	2.00530400	-2.45775000	0.10022200
C	5.20833100	-0.49225400	-0.05120500
C	2.42090200	-0.03661000	0.06391800
C	3.32437800	1.04925800	-0.13572000
C	4.71028900	0.80054300	-0.17074500
C	2.77535700	2.34715800	-0.37771700

H	3.45730100	3.17478300	-0.56037500
C	1.42534100	2.55883100	-0.40298700
C	0.51034700	1.51779700	-0.03535500
C	1.01493900	0.18882500	0.16543600
C	0.10403700	-0.92712100	0.17744400
C	0.65843000	-2.24756000	0.07739200
H	-0.01945400	-3.09547200	0.07797000
H	6.27966700	-0.66823000	-0.07899300
H	5.39081200	1.63670600	-0.31387100
H	1.00494100	3.53918200	-0.60204400
H	2.39786900	-3.47215000	0.10480600
H	4.71081100	-2.58617100	0.09965000
O	-0.74260900	1.84616200	0.08878800
C	-1.28426900	-0.67279500	0.23430900
C	-2.26381800	-1.49901400	-0.37484200
C	-1.69258400	0.60326700	0.83808300
C	-3.57900100	-1.11926100	-0.46835300
H	-1.94836500	-2.42644700	-0.84557200
C	-3.08912500	0.95690900	0.73630700
H	-1.23025000	0.80287000	1.80874800
C	-3.98256400	0.14068100	0.09249700
H	-4.29035400	-1.74875100	-0.98766500
H	-3.44723900	1.86553300	1.20792700
O	-5.27638100	0.57496800	0.05369600
C	-6.27810600	-0.27006000	-0.49082300
H	-7.21819900	0.27218100	-0.37095800
H	-6.11209600	-0.46517900	-1.55822600
H	-6.34266600	-1.22547800	0.04563700

E(B3LYP/6-31G(d)): -920.964534
E(B3LYP/6-31G(d) + ZPE): -920.681583
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -921.276255
One vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) of 9-(2,6-dimethylphenyl)-phenalenone **1c**.

C	-0.07774000	-1.99399400	0.00314300
C	1.23611900	-2.40253000	0.00383800
C	2.28601200	-1.45291600	0.00231500
C	1.94928800	-0.06600300	0.00024700
C	0.57812200	0.34629600	-0.00006300
C	-0.43751700	-0.62043800	0.00118200
H	3.88713300	-2.90936600	0.00443900
H	-0.87586500	-2.73099500	0.00419500
H	1.48136700	-3.46203300	0.00548500
C	3.65089300	-1.84814000	0.00276000
C	3.01126300	0.89466300	-0.00160500
C	4.33238700	0.46444300	-0.00118400
C	4.65682500	-0.90668900	0.00105800
H	5.12865700	1.20503500	-0.00264500
H	5.69830200	-1.21468500	0.00139800
C	2.68303100	2.30609800	-0.00406300
C	1.40497400	2.73816100	-0.00432200
H	3.50759000	3.01664700	-0.00568900
H	1.15050000	3.79352700	-0.00604700
C	0.26211300	1.81103300	-0.00163000
O	-0.88907300	2.24758000	-0.00050300
C	-1.91090700	-0.32906400	0.00036800
C	-2.60389000	-0.24988100	-1.22407000

C	-2.60437700	-0.24419900	1.22422800
C	-3.99338800	-0.08987700	-1.20426900
C	-3.99380000	-0.08443400	1.20315400
C	-4.68929700	-0.00962500	-0.00089300
H	-4.53089600	-0.02624700	-2.14758300
H	-4.53173900	-0.01649200	2.14592100
H	-5.76940800	0.11200000	-0.00132500
C	-1.86857800	-0.30009100	-2.54395700
H	-1.20725300	0.56783800	-2.65698100
H	-1.24226400	-1.19526600	-2.63735800
H	-2.57205600	-0.29364500	-3.38227600
C	-1.86939500	-0.28764600	2.54448300
H	-1.24067700	-1.18073100	2.64141000
H	-1.21053700	0.58261000	2.65416500
H	-2.57309900	-0.27983900	3.38260500

E(B3LYP/6-31G(d)): -885.121262
E(B3LYP/6-31G(d) + ZPE): -884.815002
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -885.416748
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) of the first triplet excited state of 9-(2,6-dimethylphenyl)-phenalenone **1c**, **^{3}1c***.

C	-0.08834100	-1.98626500	0.00128700
C	1.24626500	-2.39827500	0.00787900
C	2.28978100	-1.45213000	0.00849800
C	1.94774400	-0.05708500	-0.00653900
C	0.58932200	0.35005900	-0.02257100
C	-0.45666500	-0.64262200	-0.00894100
H	3.89650700	-2.89879200	0.03107600
H	-0.87514300	-2.73603800	0.00942500
H	1.48949700	-3.45751300	0.01804600
C	3.65276000	-1.84017800	0.02224800
C	3.01928700	0.91925100	-0.00512700
C	4.39468000	0.46054700	0.01176400
C	4.68940400	-0.87660600	0.02438700
H	5.18317400	1.20760800	0.01319400
H	5.72413900	-1.20784600	0.03622200
C	2.71818900	2.28327400	-0.01795200
C	1.39079800	2.70818000	-0.03887800
H	3.52722800	3.00896500	-0.01250400
H	1.13266300	3.76242500	-0.05784500
C	0.29446000	1.78855200	-0.05396200
O	-0.89295700	2.23631600	-0.10768200
C	-1.92734900	-0.33817700	0.00749500
C	-2.64476400	-0.28111900	-1.20454400
C	-2.59872500	-0.21100300	1.24061200
C	-4.03106600	-0.09897200	-1.16402300
C	-3.98615700	-0.02981600	1.24177200
C	-4.70310900	0.02432900	0.04950100
H	-4.58520400	-0.04951500	-2.09860000
H	-4.50514100	0.07152000	2.19221100
H	-5.78095400	0.16421100	0.06564200
C	-1.93576900	-0.37849600	-2.53609600
H	-1.22904900	0.45040800	-2.66559600
H	-1.36092800	-1.30707500	-2.63297600
H	-2.65162800	-0.33829200	-3.36303000
C	-1.84313800	-0.24538000	2.54985600
H	-1.25801700	-1.16544700	2.66492000

H	-1.13830900	0.59211100	2.62284500
H	-2.53081000	-0.17567600	3.39843300

E(UB3LYP/6-31G(d)): -885.054272
E(UB3LYP/6-31G(d) + ZPE): -884.751624
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -885.348531
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the transition state connecting ^{3}**1c*** and ^{3}**3c***.

C	-3.77221100	-1.69596400	0.00003600
C	-2.38116000	-1.42054400	0.00003600
C	-1.35086000	-2.40705000	0.00007900
C	-4.69593500	-0.64831600	-0.00000800
C	-1.98841000	-0.04886000	-0.00001200
C	-2.92337400	1.02994600	-0.00005800
C	-4.29847600	0.69132600	-0.00005400
C	-2.40163600	2.35791600	-0.00010400
H	-3.10465200	3.18754100	-0.00013900
C	-1.03169900	2.63854400	-0.00010700
C	-0.11716400	1.57210200	-0.00006100
C	-0.61911300	0.25058900	-0.00001400
C	0.38711400	-0.72275900	0.00002900
C	0.00711900	-2.06949100	0.00007500
H	0.75580900	-2.85810500	0.00010900
H	-5.75768000	-0.88236800	-0.00000700
H	-5.04635700	1.48042400	-0.00008800
H	-0.67525700	3.66363300	-0.00014300
H	-1.63591500	-3.45613100	0.00011500
H	-4.11597400	-2.72721400	0.00007100
O	1.21253500	1.64489300	-0.00005800
C	1.76664100	-0.11243900	0.00001600
C	2.52877700	-0.16659100	1.25936800
C	2.52880000	-0.16669500	-1.25931800
C	3.90713300	-0.12998600	1.21963800
C	3.90715500	-0.13009100	-1.21956700
C	4.60589600	-0.10493500	0.00004100
H	4.46408500	-0.13407600	2.15333900
H	4.46412400	-0.13426300	-2.15325800
H	5.69182600	-0.07919400	0.00004900
C	1.78409700	-0.19495500	-2.56408800
H	1.13306400	-1.07372300	-2.64060900
H	1.13838400	0.68657200	-2.65994300
H	2.47824900	-0.20392100	-3.40959800
C	1.78405200	-0.19474100	2.56412500
H	1.13835600	0.68680600	2.65990600
H	1.13299900	-1.07349100	2.64070100
H	2.47818900	-0.20366300	3.40964800

E(UB3LYP/6-31G(d)): -885.045661
E(UB3LYP/6-31G(d) + ZPE): -884.742668
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -885.339295
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the transition state connecting ^{3}**1c*** and ^{3}**4c***.

C	-3.82032400	1.57108000	0.35474200

C	-2.42510600	1.33064100	0.33648200
C	-1.47477300	2.33292300	0.66788600
C	-4.72079200	0.56554600	0.01455400
C	-1.94812400	0.03050200	-0.03229500
C	-2.88494900	-0.99398300	-0.38226900
C	-4.26679900	-0.70025100	-0.35142700
C	-2.38101000	-2.27485900	-0.74235700
H	-3.08673200	-3.05823700	-1.00847700
C	-1.02778500	-2.54558600	-0.73929800
C	-0.08100800	-1.54448300	-0.41561000
C	-0.54566800	-0.23003200	-0.05962000
C	0.38141200	0.81064100	0.25759000
C	-0.11421000	2.07464000	0.61741500
H	0.58640000	2.85848000	0.88960500
H	-5.78819000	0.76979800	0.03289300
H	-4.97601700	-1.48007300	-0.61773600
H	-0.65066000	-3.53017300	-0.99738200
H	-1.82996000	3.31663500	0.96404000
H	-4.17951600	2.55762000	0.63668500
O	1.20297600	-1.85945300	-0.44361000
C	1.81967000	0.49560800	0.17849600
C	2.72760000	1.24153400	-0.59400200
C	2.23993400	-0.76348700	0.78550500
C	4.03234600	0.75358000	-0.76578900
C	3.58750800	-1.20610300	0.56034800
C	4.45512200	-0.46745200	-0.20510700
H	4.72573700	1.32208400	-1.38054000
H	3.90654300	-2.13340200	1.02750800
H	5.47265800	-0.81093200	-0.37013700
C	1.61485500	-1.24147000	2.08157100
H	1.83334600	-2.30221100	2.23403100
H	2.05119300	-0.68019600	2.91816900
H	0.53471200	-1.09683000	2.11263800
C	2.33985000	2.52125800	-1.30365600
H	1.32503300	2.46911000	-1.70794700
H	2.37586700	3.38967300	-0.63398800
H	3.02928100	2.72279600	-2.12943600

E(UB3LYP/6-31G(d)): -885.043906
E(UB3LYP/6-31G(d) + ZPE): -884.740024
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -885.337485
One vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for triplet biradical ^{3}**3c***.

C	-0.11904600	-2.02514600	0.00008100
C	1.22687500	-2.42388900	0.00009000
C	2.31041300	-1.49184200	0.00004900
C	1.98652400	-0.10474200	-0.00000400
C	0.63673300	0.24425800	-0.00001100
C	-0.42148300	-0.66178300	0.00002900
H	3.99992300	-2.86176800	0.00009300
H	-0.90267100	-2.77835500	0.00011400
H	1.45978500	-3.48584200	0.00013100
C	3.69053800	-1.81977300	0.00005400
C	2.95027400	0.94650000	-0.00005000
C	4.31213400	0.55298600	-0.00004100
C	4.65154900	-0.80390600	0.00001000
H	5.09420200	1.30804100	-0.00007400
H	5.70328900	-1.07939600	0.00001600

C	2.46402300	2.28931100	-0.00010000
C	1.09553100	2.61459600	-0.00010700
H	3.18903500	3.09931500	-0.00013500
H	0.77309400	3.65075600	-0.00014700
C	0.17596400	1.56680200	-0.00006200
O	-1.18338000	1.60423500	-0.00005800
C	-1.72082100	0.15885800	0.00000100
C	-2.51916100	-0.00628500	1.27602300
C	-2.51917200	-0.00638300	-1.27600100
C	-3.84351400	-0.35630400	1.22244200
C	-3.84352500	-0.35639500	-1.22238100
C	-4.52455100	-0.54927000	0.00004100
H	-4.38796400	-0.48260500	2.15593000
H	-4.38798500	-0.48276300	-2.15585500
H	-5.57436500	-0.82526800	0.00005600
C	-1.80968300	0.22818200	2.57940500
H	-0.95773500	-0.45201200	2.70682200
H	-1.41121600	1.24890900	2.63245500
H	-2.49032500	0.08408200	3.42388900
C	-1.80971000	0.22800100	-2.57940700
H	-1.41119900	1.24870800	-2.63250500
H	-0.95779500	-0.45223400	-2.70681600
H	-2.49037600	0.08389800	-3.42387100

E(UB3LYP/6-31G(d)): -885.049124
E(UB3LYP/6-31G(d) + ZPE): -884.745137
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -885.342180
No vibrational mode with imaginary frequency.

Optimized geometry (UB3LYP/6-31G*) for the first triplet excited state of **4c**, ^{3}**4c***.

C	-3.84915000	1.61385700	0.24962200
C	-2.45089400	1.36621400	0.24980300
C	-1.49401700	2.37116800	0.53181400
C	-4.75071000	0.59299900	-0.02979400
C	-1.98269400	0.04495600	-0.03793900
C	-2.91943000	-0.99945900	-0.32209200
C	-4.30209200	-0.69737600	-0.31404700
C	-2.41916100	-2.30006600	-0.59852200
H	-3.12331100	-3.09763900	-0.82093600
C	-1.05960400	-2.57071500	-0.56681200
C	-0.14238700	-1.55215000	-0.28823900
C	-0.58177100	-0.21967600	-0.04601300
C	0.36289700	0.83021800	0.16995800
C	-0.12945400	2.10506100	0.48792600
H	0.56575300	2.90126900	0.72780300
H	-5.81737400	0.80164600	-0.02743700
H	-5.01498300	-1.48882800	-0.53104800
H	-0.67921900	-3.57087500	-0.74957900
H	-1.83969500	3.37040400	0.78429200
H	-4.20498200	2.61707400	0.46984900
O	1.17427100	-1.87909800	-0.25739400
C	1.78775000	0.47303500	0.05167400
C	2.79153300	1.28198900	-0.44758700
C	2.07657800	-0.96065200	0.47386500
C	4.11739600	0.76778400	-0.57585900
C	3.46063600	-1.43242200	0.15838200
C	4.42453600	-0.57936400	-0.29412500
H	4.89410700	1.42499100	-0.95621700

H	3.66706400	-2.48079100	0.35423500
H	5.43544000	-0.94195100	-0.46366000
C	1.81236200	-1.17372400	1.98505300
H	1.99775300	-2.22079100	2.24616200
H	2.48327400	-0.54019500	2.57346300
H	0.78036800	-0.92340200	2.24642800
C	2.56622400	2.69856900	-0.93611200
H	1.57900700	2.82433800	-1.38882800
H	2.65191200	3.43396400	-0.12521000
H	3.31943500	2.96209800	-1.68592800

E(UB3LYP/6-31G(d)): -885.057453
E(UB3LYP/6-31G(d) + ZPE): -884.752315
E(UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)): -885.349984
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for **4c**.

C	-3.81134300	1.70066900	0.14649700
C	-2.44722100	1.41657900	0.11765900
C	-1.43663300	2.44122500	0.19624400
C	-4.76532600	0.67499900	0.02702100
C	-2.00814000	0.06537200	-0.01854000
C	-2.98037800	-0.96980400	-0.17532200
C	-4.35804100	-0.63496400	-0.13909500
C	-2.52915500	-2.29944300	-0.39397700
H	-3.26278500	-3.09124600	-0.52314300
C	-1.18653600	-2.58927300	-0.43958000
C	-0.23521300	-1.56721800	-0.22710800
C	-0.61274600	-0.23703500	-0.02648300
C	0.40842400	0.81439900	0.03672900
C	-0.10824000	2.16627200	0.13026700
H	0.57859600	2.99223300	0.21548000
H	-5.82387800	0.91809500	0.05253100
H	-5.09195400	-1.42914600	-0.25331400
H	-0.82372100	-3.59844900	-0.60652700
H	-1.76356100	3.47236600	0.31071400
H	-4.13595400	2.73300600	0.25389000
O	1.06287100	-1.93559200	-0.26493900
C	1.75308700	0.44397600	0.00472600
C	2.91256200	1.28702100	-0.23298400
C	2.03424600	-1.03422400	0.34566400
C	4.14185500	0.70790700	-0.42563900
C	3.34680600	-1.55770100	-0.16367300
C	4.35042300	-0.71849600	-0.46195800
H	4.98934600	1.35128700	-0.64641100
H	3.44351300	-2.63829000	-0.21058500
H	5.32238200	-1.09793900	-0.76748900
C	1.96366200	-1.22163800	1.87890000
H	2.12954600	-2.27324000	2.13857200
H	2.74067700	-0.61494300	2.35440700
H	0.99078900	-0.90439800	2.26877200
C	2.84733100	2.79299100	-0.37989800
H	2.15148200	3.10224900	-1.16791000
H	2.54104000	3.29141300	0.54785800
H	3.83497100	3.18204900	-0.64404800

E(B3LYP/6-31G(d)): -885.081907
E(B3LYP/6-31G(d) + ZPE): -884.773668

E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -885.375753
No vibrational mode with imaginary frequency.

Optimized geometry (B3LYP/6-31G*) for the transition state connecting **4c** and **1c**.

C	-3.81370700	1.57675000	0.31244500
C	-2.43318000	1.32011300	0.33088100
C	-1.46685300	2.34241200	0.59476900
C	-4.72303900	0.57669800	-0.03175300
C	-1.95402400	0.00801600	0.03740100
C	-2.88940500	-0.99309000	-0.36824800
C	-4.26261800	-0.68859300	-0.38635100
C	-2.38449500	-2.25736900	-0.80889800
H	-3.09197900	-3.00932100	-1.15105700
C	-1.04563600	-2.52772700	-0.80855800
C	-0.11412000	-1.60185500	-0.23264000
C	-0.55746600	-0.28040700	0.11090200
C	0.39898300	0.77844100	0.30149500
C	-0.12529600	2.09553300	0.52695100
H	0.56946100	2.89893300	0.73560400
H	-5.78753100	0.79193000	-0.04720400
H	-4.96633900	-1.45681000	-0.69829700
H	-0.65430600	-3.48653000	-1.13288500
H	-1.82184700	3.34048000	0.84165100
H	-4.16705200	2.57675300	0.55257300
O	1.09149600	-2.02365300	-0.02031700
C	1.79581600	0.48680800	0.17858900
C	2.72422800	1.30666500	-0.54671100
C	2.22222100	-0.83791000	0.67566700
C	3.97192900	0.80140700	-0.86170900
C	3.52754400	-1.31212300	0.23971600
C	4.35668900	-0.51460400	-0.48732500
H	4.65196000	1.40088900	-1.46002800
H	3.82790400	-2.30843100	0.55141200
H	5.33745000	-0.88188100	-0.78164400
C	1.90015100	-1.14878800	2.13146000
H	2.05477900	-2.21249700	2.33834800
H	2.57856100	-0.57097700	2.77123200
H	0.87458100	-0.87637900	2.39517900
C	2.37178500	2.67819200	-1.08485500
H	1.38494800	2.69926600	-1.55914500
H	2.37026100	3.44664600	-0.30129000
H	3.11013900	2.98573500	-1.83127800

E(B3LYP/6-31G(d)): -885.069312
E(B3LYP/6-31G(d) + ZPE): -884.763244
E(B3LYP/cc-pVTZ//B3LYP/6-31G(d)): -885.363111
One vibrational mode with imaginary frequency.