Supplementary information for the paper

Carbon dioxide as a primary oxidant and a C1 building block

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Experimental details

General

Instruments: All infrared spectra were obtained in KBr pellets using a ThermoNicolet Avatar 330 FT-IR. UV-Vis spectra were recorded at an Agilent 8453 spectrometer. NMR spectra were recorded on a Bruker Avance 400 (400 MHz) instrument. Chemical shifts (δ) were reported in parts per million (ppm), downfield from internal TMS or H_3PO_4. In the case of 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole derivates, UV and NMR spectra were recorded under argon atmosphere. Melting points were obtained by using a calibrated melting point microscope. Elemental analyses were performed on a Carlo Erba 1012 apparatus. Field desorption mass (FD-MS) spectra were measured on an Agilent 6890 N Network GC system with an Agilent 5973 Network MS mass spectrometer equitted with an DB-5MS UI column. Gaschromatographic (GC) analyses and the kinetic measurements were carried out on a HP 4890D instrument with flame ionization detector equipped with an Equity-1 capillary column. HPLC was measured on a *Jasco* LC-2000PLUS SERIES HPLC SYSTEM with a Gemini NX C18 250x4.6 mm column, 25 °C, eluent water:acetonitrile 20:80, eluent speed 0.5 mL/min, injected volume 20 μL. Cyclic voltammograms were taken on a VoltaLab PST006 potentiostat with Voltamaster 4 software for data processing using a three-electrode configuration composed of Pt-wire counter electrode, glassy carbon working electrode and an Ag/AgCl (3M) reference electrode. The potentials were referenced versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple. The CVs were measured in argon-saturated acetonitrile using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte.

Materials and Methods: Solvents, reagents and starting materials were purchased from commercial sources and were used as received with the exception of acetonitrile, which was distilled under an atmosphere of argon from calcium hydride prior to use.[1] All manipulations were performed under argon by standard Schlenk-techniques. 9,10-Phenanthrenequinone[2] and 2,7-*tert*-butyl-9,10-phenanthrenequinone[3] was prepared from phenanthrene and 2,7-di-*tert*-butylphenanthrene by CrO_3 oxidation. 2,7-Dinitro-9,10-phenanthrenequinone[4] was prepared by nitration of 9,10-phenanthrenequinone, and 2,7-dibromo-9,10-phenanthrenequinone[5] was prepared by reaction between NBS (*N*-bromosuccinimide) and 9,10-phenanthrenequinone.

General procedure for synthesis 9,10-phenanthrenequinone monoimines (1a-d)[6]

2,7-Derivates of phenanthrenequinone (10 mmol) were dissolved in a mixture of $CHCl_3$ (30 mL) and ethanol (60 mL). NH_3(g) was bubbled through the solution at reflux temperature for 2 h. After cooling yellow needles were separated and dried in *vacuum*.

2,7-Di-*tert*-butyl-9,10-phenanthrenequinone monoimine (1a): The title compound was prepared according to the general procedure. Yield: 2.31 g (72%). m.p. 174-175 °C; FTIR (KBr) ν =3199(m) (N-H), 3077(w) (C-H), 2958(s) (C-H), 1669 cm^{-1} (s) (C=O); UV-Vis(CH_3CN), λ_{max}(lgε) = 213(4.67), 265(4.86), 274(4.83), 315(3.74), 420 nm(3.53); MS (70 eV): *m*/*z* (%): 319.2(100) [M^+]. Elemental analysis for $C_{22}H_{25}NO$ calc.: C 82.72, H 7.89, N 4.38, O 5.01%, found: C 82.70, H 7.82, N 4.35, O 4.97%.

9,10-Phenanthrenequinone monoimine (1b): The title compound was prepared according to the general procedure. Yield: 1.55 g (75%). m.p. 165-167°C; FTIR (KBr): ν =3199(m) (N-H), 1674(s) (C=O), 1589, 1451, 1282, 1251, 1227, 1122, 1011, 942, 923, 897, 758, 714, 696, 534, 433 cm^{-1}; UV-Vis(CH_3CN): λ_{max}(lgε) = 213(4.44), 257(4.49), 265(4.49), 314(3.54), 393nm (3.21); MS (70 eV): *m*/*z* (%): 207.2(89) [M^+]; Elemental analysis for $C_{14}H_9NO$ calc.: C 81.14, H 4.38, N 6.76, O 7.72%, found: C 81.04, H 4.37, N 6.76, O 7.67%.

2,7-Dibromo-9,10-phenanthrenequinone monoimine (1c): The title compound was prepared according to the general procedure. Yield: 2.88 g (79%). m.p. 235-237 °C; FTIR (KBr): ν =3199(m) (N-H), 1677(s) (C=O), 1077(m) (C_{arom}-Br), 1033 cm^{-1}(w) (C_{arom}-Br); UV-Vis(CH_3CN), λ_{max}(lgε) = 191(4.42), 213(4.41), 276(4.65), 411nm (3.39); MS (70 eV): *m*/*z*(%)*:* 365.5(100) [M^+]; Elemental analysis for $C_{14}H_7Br_2NO$ calc.: C 46.07, H 1.93, N 3.84, O 4.38%, found: C 46.02, H 1.91, N 3.79, O 4.37%.

2,7-Dinitro-9,10-phenanthrenequinone monoimine (1d): The title compound was prepared according to the general procedure. Yield: 1.95 g (66%). m.p. 291-293°C; FTIR (KBr): ν = 3211 (m, N-H stretch), 3166, 1674(s, C=O stretch), 1516, 1348 cm^{-1}; UV-Vis(CH_3CN), λ_{max}(lgε) = 204(4.36), 224(4.36), 296(4.41), 369(3.80) nm. Elemental analysis for $C_{14}H_7N_3O_5$ calc.: C 56.57, H 2.37, N 14.14, O 26.92%, found: C 56.51, H 2.35, N 14.08, O 26.84%. MS *m*/*z:* 296.9 (M^+).

General procedure for synthesis 1,3,2-oxazaphospholes (2a-d)

In an argon flushed Schlenk vessel **1a-d** (2 mmol) and triphenylphosphine (0.53 g, 2 mmol) were dissolved in argon saturated acetonitrile (10 mL) and refluxed for 2 h. After cooling the precipitate were filtered off under argon and dried in *vacuum*.

2,3-Dihydro-2,2,2-triphenyl-2,7-di-*tert*-butylphenanthro[9,10-d]-1,3,2λ⁵-oxazaphosphole (2a): The reaction was carried out according to the general procedure. The product was obtained as a brown solid in 55% (0.64 g) yield. m. p. 258-261°C; FTIR (KBr): ν = 3452(m, N-H stretch), 3051, 2954(s, C-H stretch), 2905(m, C-H stretch), 2858(m, C-H stretch), 1612, 1586, 1435, 1365, 1306, 1187, 1110 cm^{-1}; ^1H-NMR (CD_3CN, 25°C): δ = 8.59-8.51 (m, ar., 2H); 8.03 (brs, NH, 1H); 7.77-7.34 (m, ar., 17H); 7.23 (s, ar., 2H); 1.45 (s, *t*Bu, 9H); 1.26 (s, *t*Bu, 9H);^{31}P-NMR (162 MHz, CD_3CN, 25°C): δ = 29.08, 21.92; UV-Vis(CH_3CN): $\lambda_{max}(\lg\varepsilon)$ = 262(4.64), 274(4.61), 335(3.95), 413(3.48), 526 nm (3.13); MS (70 eV): *m*/*z*(%): 582.1 (100) [M^+]; Elemental analysis for $C_{40}H_{40}NOP$ calc.: C 82.59, H 6.93, N 2.41, O 2.75%, found:C 82.52,H 6.89, N 2.37, O 2.71%.

2,3-Dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ⁵-oxazaphosphole (2b).[7]

2,3-Dihydro-2,2,2-triphenyl-2,7-dibromophenanthro[9,10-d]-1,3,2λ⁵-oxazaphosphole (2c): The reaction was carried out according to the general procedure. The product was obtained as a red solid in 57% (0.72g) yield. m. p. 214-216°C; FTIR (KBr) ν = 3407(m, N-H stretch), 3052, 1618, 1588, 1414, 1366, 1311, 1086, 1073(m, C_{arom}-Br stretch), 1057, 1025, 993cm^{-1}; ^1H-NMR (CD_3CN, 25°): δ = 7.68-7.21 (m, ar., 22H); ^{31}P-NMR (162 MHz, CD_3CN, 25°C): δ = 29.24; UV-Vis(CH_3CN), λ_{max} ($\lg\varepsilon$) = 268(4.54), 282(4.46), 346(3.88), 414(3.30), 500(2.89), 536nm (2.87). MS (70 eV): *m*/*z*(%)*:* 627.3 (100) [M^+]; Elemental analysis for $C_{32}H_{22}Br_2NOP$ calc.: C 61.27, H 3.53, N 2.32, O 2.55%, found:C 61.20, H 3.49, N 2.31, O 2.52%.

2,3-Dihydro-2,2,2-triphenyl-2,7-dinitrophenanthro[9,10-d]-1,3,2λ⁵-oxazaphosphole (2d): The reaction was carried out according to the general procedure. The product was obtained as a purple solid in 55% (0.61 g) yield. m. p. 134-135°C; FTIR (KBr): ν = 3419(m) (N-H), 3314(m), 1602(m), 1508(s), 1434(s), 1341 cm^{-1} (s); ^1H-NMR (CD_3CN, 25°C): δ = 7.67-7.23 (m, ar., 22H). ^{31}P-NMR (162 MHz, CD_3CN, 25°C) δ = 29.64; UV-Vis(CH_3CN): $\lambda_{max}(\lg\varepsilon)$ = 322(4.53), 540 nm (3.30); MS (70 eV): *m*/*z*(%): 559.8 (100) [M^+]; Elemental analysis for $C_{32}H_{22}N_3O_5P$ calc.: C 68.69, H 3.96, N 7.51, O 14.30%, found: C 68.64, H 3.90, N 7.45, O 14.22%.

Preparation of *3H*-phenanthro[9,10-d]oxazol-2-ones (general procedure) at reflux temperature „*a)*”, at room temperature „*b)*” and in one-pot route „*c)*”.

3*H*-Phenanthro[9,10-d]oxazol-2-one (4b): *a)* In argon-saturated acetonitrile (80 mL) **2b** (4.70 g, 10 mmol) was dissolved. The argon atmosphere was replaced by carbon dioxide and the mixture was refluxed for 3 h. It was cooled down to room temperature, filtered and the solid material was refluxed in 500 mL ethanol and hot filtered. From the filtrate on standing pinkish needles separated, which were filtered off and dried in vacuum to give 1.83 g (78%) **4b**. b*)* In argon-saturated acetonitrile (80 mL) **2b** (4.70 g, 10 mmol) was dissolved. The argon atmosphere was replaced by carbon dioxide and the mixture was stirred at room temperature for 24 h. The previously described workup gives 1.69 g (72%) **4b**. *c)* In 80 ml argon-saturated acetonitrile **1b** (2.07 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) was dissolved. The argon atmosphere was replaced by carbon dioxide and the mixture was refluxed for 3 h. The previously described workup gives 1.86 g (79%) **4b**. m. p. 319-21°C; FTIR (KBr): ν = 3446(m) (N-H), 3148(m), 3075(m), 1750(vs) (C=O), 1618(m), 1538(w), 1451(m), 1375(s), 1052(m), 1031(m), 933(s), 745(s) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6, 25°C): δ = 8.89 (t, ar., 2H); 8.10 (dd, ar., 1H); 8.00 (dd, ar., 1H); 7.78-7.62 (m, ar., 4H). ^{13}C-NMR (400 MHz, DMSO-d_6, 25°C): δ = 155.80 (C=O), 135.17, 128.40, 128.13, 127.86, 127.06, 126.66, 125.94, 124.69, 124.55, 122.90, 122.18, 120.51, 120.22, 119.7. MS (70 eV): *m*/*z*(%): 235.1(100) [M^+]; Elemental analysis for $C_{15}H_9NO_2$ calc.: C 76.66, H 3.86, N 5.95, O 13.60%, found: C 76.50, H 3.75, N 5.85%.

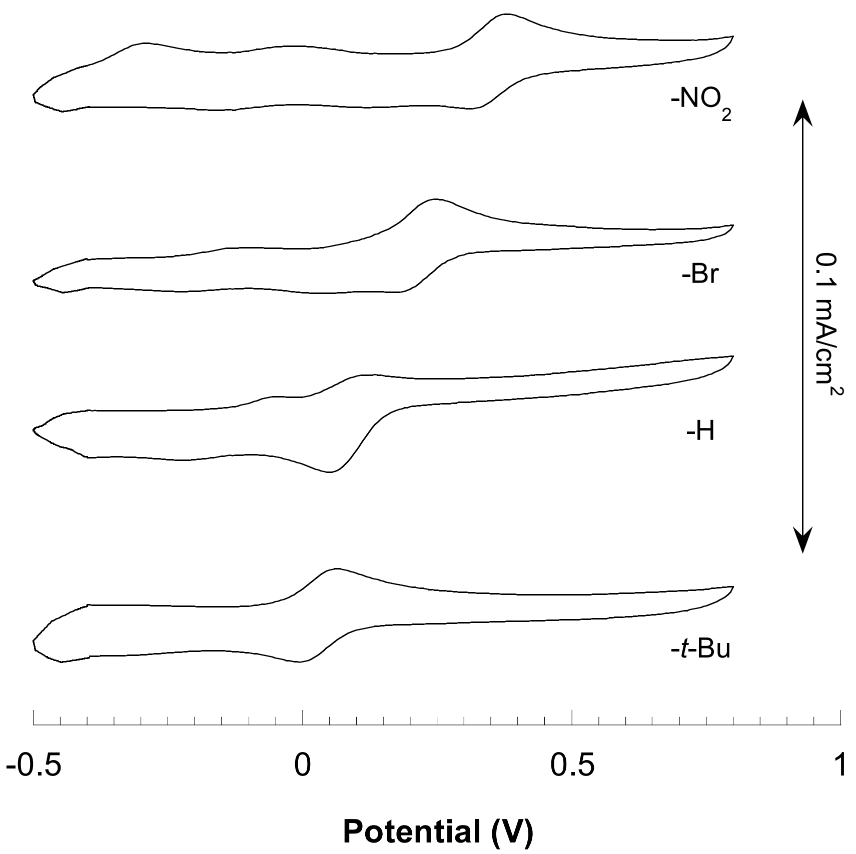
Identification of $OPPh_3$: The filtrate from the crude product *a)* was concentrated under reduced pressure and flash chromatographed on silica gel (eluent: EtOAc-petrolether1:1). The colored fragments were eliminated and the remaining triphenylphosphine oxide was washed out with methanol. The solvent evaporated and the remaining solid identified as triphenylphosphine oxide (1.05 g, 38%) compared with an authentic sample (TLC, mixed melting point, FTIR).

2,7-Di-*tert*-butylphenantro[9,10-d][1,3]oxazol-2(3*H*)-on (4a): According to the method *c)* **2a** (0.64 g, 2 mmol) and triphenylphosphine (0.53 g, 2 mmol) were dissolved in acetonitrile (20 mL) under argon. The argon atmosphere was replaced by carbon dioxide and the mixture refluxed for 3 h. Workup as previously described and recrystallized from ethanol gave colorless needles of **4a** (0.28 g 80%). m. p. 379-381°C; FTIR (KBr): ν = 3448(m) (N-H), 3154(m), 3028(w), 3148(m), 2959(s), 2901(m), 2864(w), 1758(vs) (C=O), 1625(m), 1524(w), 1479(m), 1427(m), 1375(s), 1263(m), 1054(m), 932(s), 878(m), 812(s) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6, 25°C): δ = 8.74 (dd, ar., 2H); 8.14 (d, ar., 1H); 7.89 (d, ar.1H); 7.72 (ddd, ar, 2H); 1.42 (s, t-Bu, 18H). ^{13}C-NMR (400 MHz, DMSO-d6, 25°C): δ = 155.79 (C=O), 150.57, 150.48, 135.38, 125.60, 124.90, 124.76, 124.27, 124.13, 123.10, 120.08, 119.81, 118.10, 114.99, 31.64 (*t*-Bu), 31.54 (*t*-Bu); MS (70 eV): *m*/*z*(%): 347.2(100) [M^+]; Elemental analysis for $C_{23}H_{25}NO_2$ calc.: C 79.50, H 7.25, N 4.03, O 9.21%, found: C 79.45, H 7.12, N 3.94, O 9.20%.

References:

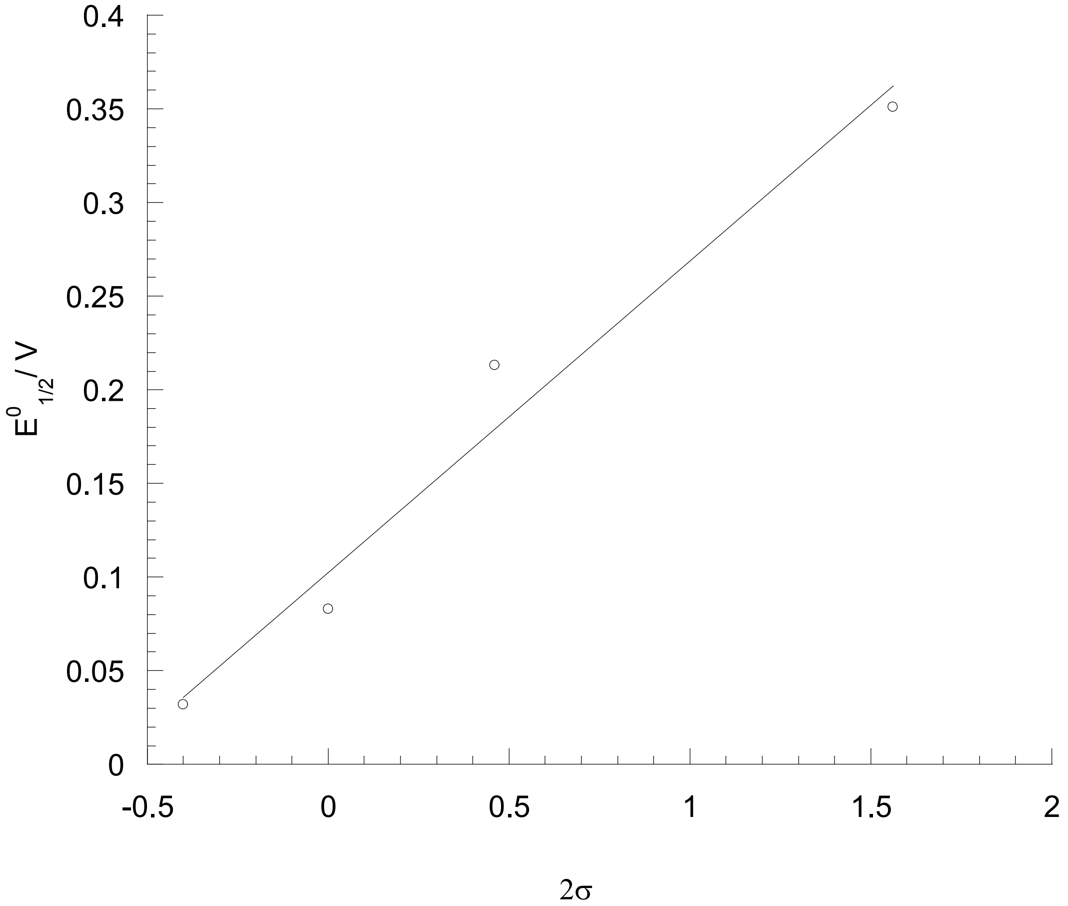
1. W. Armarego, C. Chai, 6th ed., *Purification of Laboratory Chemicals*, Elsevier, Oxford, **2009**.
2. R. Anschütz, G. Schultz, *Liebigs Ann. Chem.* **1879**, *196*, 32-57.
3. A. Berg, J. H. Jakobsen, S.R. Johansen, *Acta Chem. Scand.***1969**, *23*, 567-575.
4. T. K. Mukherjee, *J. Phys. Chem.* **1967**, *71*, 2277-2282.
5. M. Hanif, L. Ping, L. Mao, Z. Yan, Y. Zengh, X. Zengqi, M. Yuguang, L. Di, L. Jinghong, *Polym. Internat.* **2007**, *56*, 1507-1513.
6. É.Balogh-Hergovich, G. Speier, Z. Tyeklár, *Synthesis,* **1982,** *9,* 731-732.
7. G. Speier, Z. Tyeklár, V. Fülöp, L. Párkányi, *Chem. Ber.* **1988**, *121*, 1685-1688.

SFigure 1. The CVs of 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole derivatives (**2a-d**). The 2,7-dibromo- and 2,7-dinitro derivatives did not react under the investigated conditions. E°$_{1/2}$ are given against Fc/Fc$^+$.

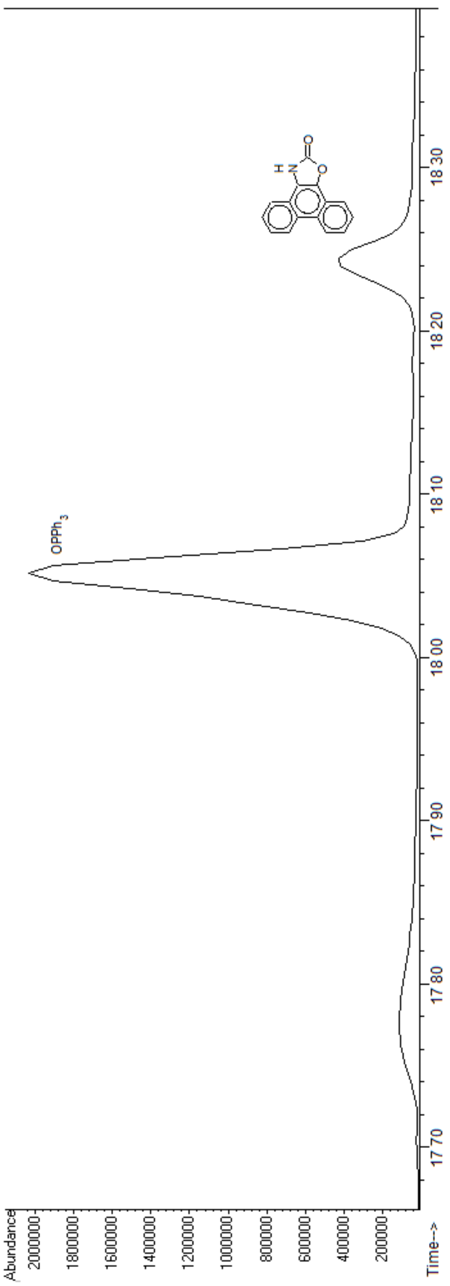


Derivative	E$^0_{1/2}$ (V)
-*t*Bu	0.032
-H	0.083
-Br	0.213
-NO$_2$	0.351

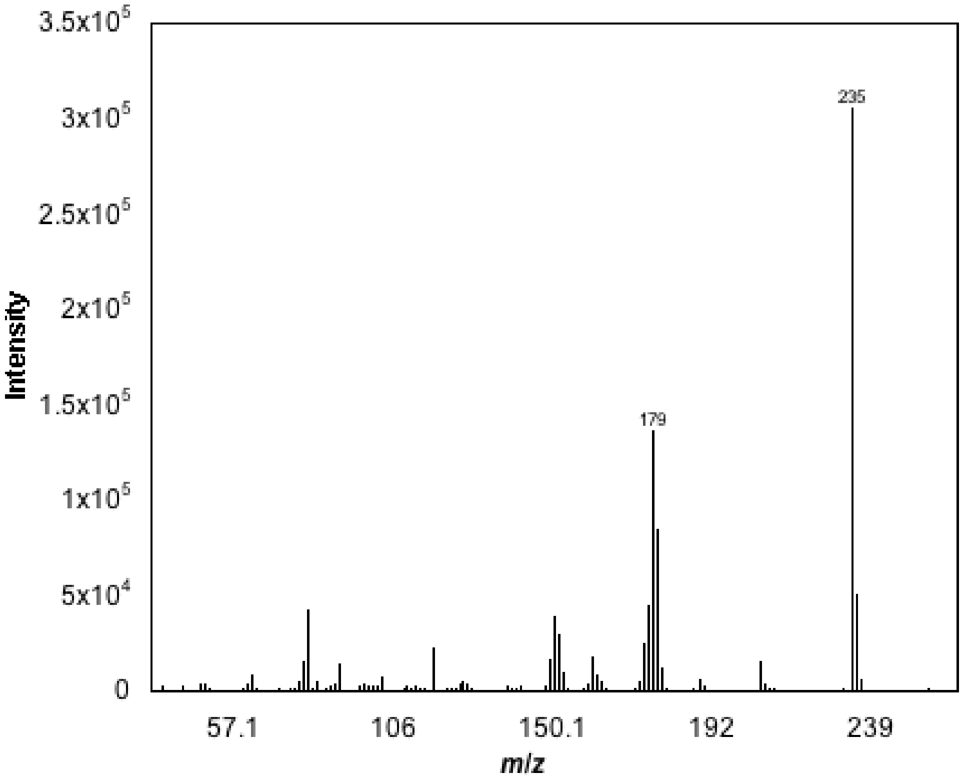
SFigure 2. The redox potentals (**E^0 $_{½}$**) of **2a-d** *vs* their 2σ values.



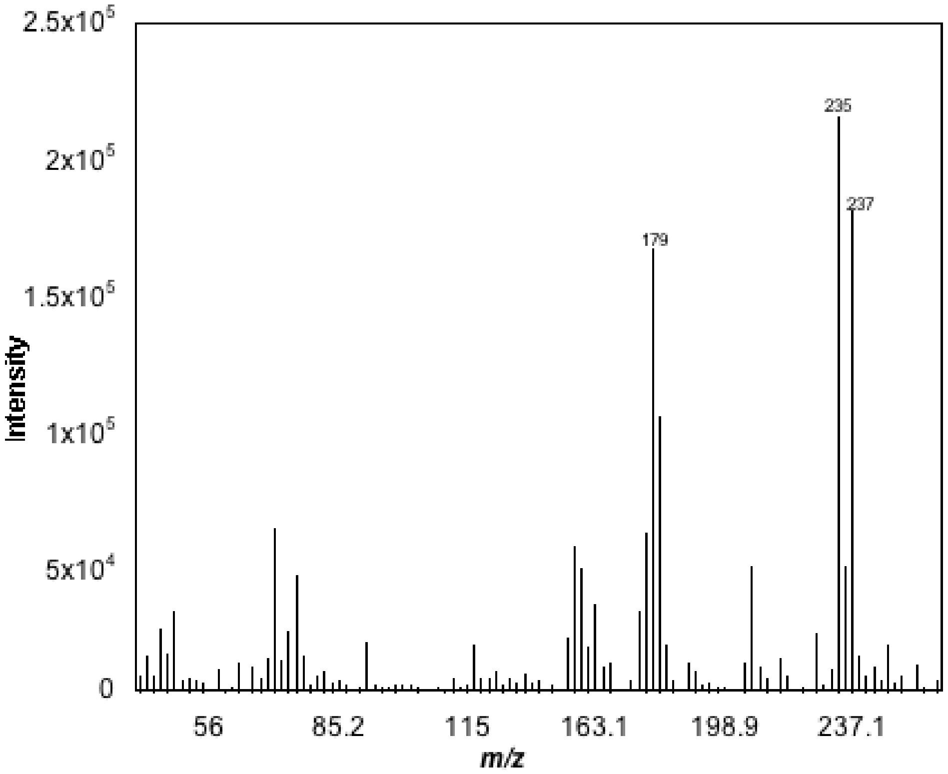
SFigure 3. The gas chromatogram of the reaction mixture between 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole (**2b**) and CO_2 at the end of the synthetic procedure *a)*. Injected volume: 1 μL, 10°C/min from 100°C.



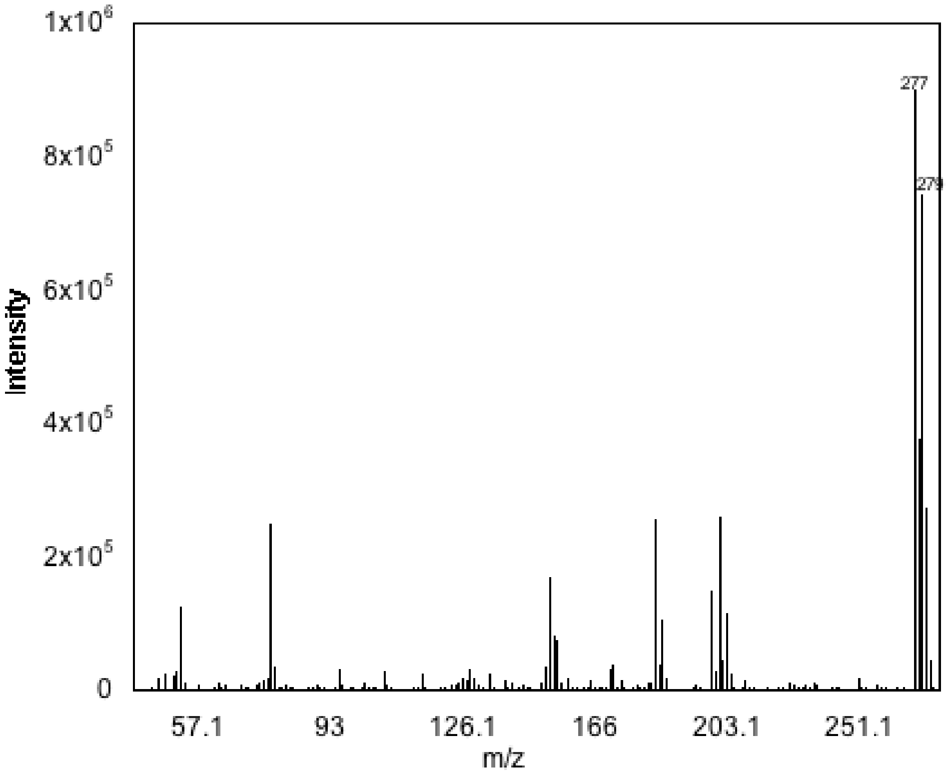
SFigure 4. The MS of spectrum of phenanthro[9,10-d][1,3]oxazol-2(3*H*)-one (**4b**) from the reaction of 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole with $C^{16}O_2$ in acetonitrile.



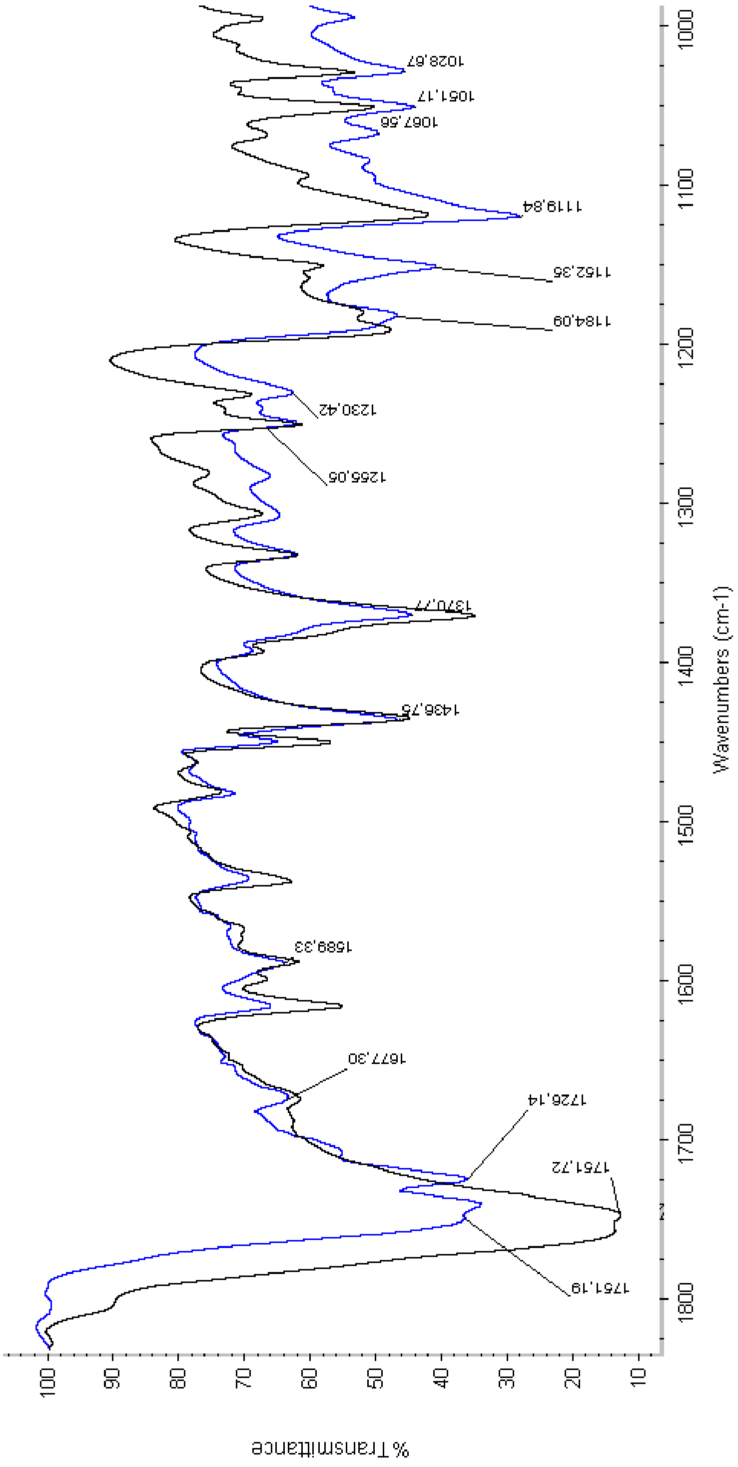
SFigure 5. The MS spectrum of phenanthro[9,10-d][1,3]oxazol-2(3*H*)-one (**4b**) prepared from 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole and an isotope mixture of $C^{16}O_2$:$C^{18}O_2$ (~50:50).



SFigure 6. The MS spectrum of a mixture of $^{16}OPPh_3$ and $^{18}OPPh_3$ mixture of the reaction product from the reaction of 2,3-dihydro-2,2,2-triphenylphenanthro[9,10-d]-1,3,2λ^5-oxazaphosphole with $C^{16}O_2$:$C^{18}O_2$ (~50:50) in MeCN.



SFigure 7. The IR spectra of the products of the reaction of **2b** with CO_2. Blue line is related to the $C^{16}O_2$:$C^{18}O_2$ (~50:50) experiment, black to the $C^{16}O_2$ experiment. $\nu_{C=}{}^{16}{}_{O}$: 1752 cm^{-1}; $\nu_{C=}{}^{18}{}_{O}$: 1726 cm^{-1}; $\nu_{P=}{}^{16}{}_{O}$: 1184 cm^{-1}; $\nu_{P=}{}^{18}{}_{O}$: 1152 cm^{-1}.



Kinetics

A Schlenk tube, containing the described concentrations of **2b** in acetonitrile, fitted with septum and excess of CO_2 was placed in a thermostated bath. The reaction (1) was monitored with GC in the presence of naphthalene as an internal standard. The GC analysis was performed almost immediately after sample acquisition. The concentration of [**2b**] was determined vs the time. The velocity of reaction (1) is given by equation (2). By using CO_2 in excess,(1) becomes a pseudo-first order reaction represented by equation (3) and (4).

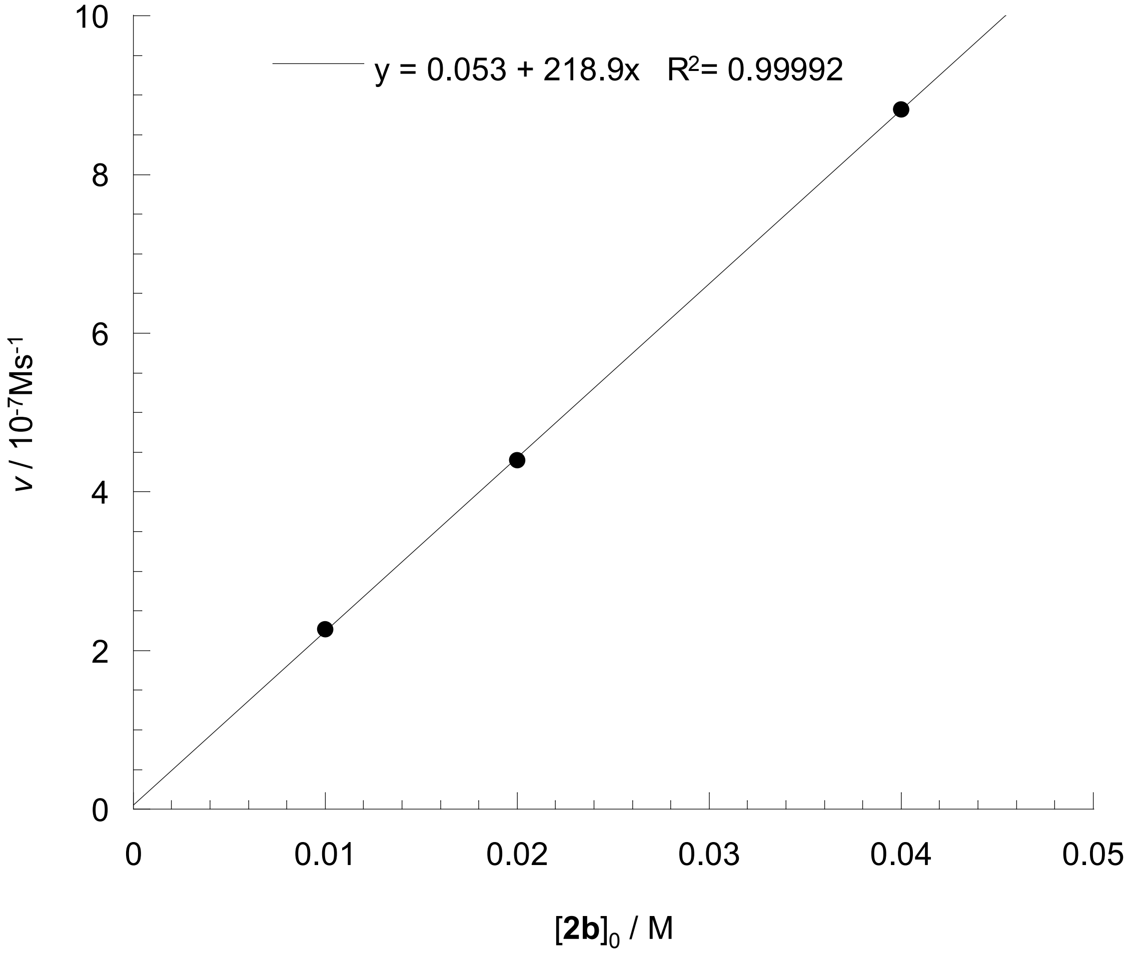
(1) $\mathbf{2b} + CO_2 \rightarrow \mathbf{4b} + OPPh_3$

(2) $v = k_2[CO_2][\mathbf{2b}]$

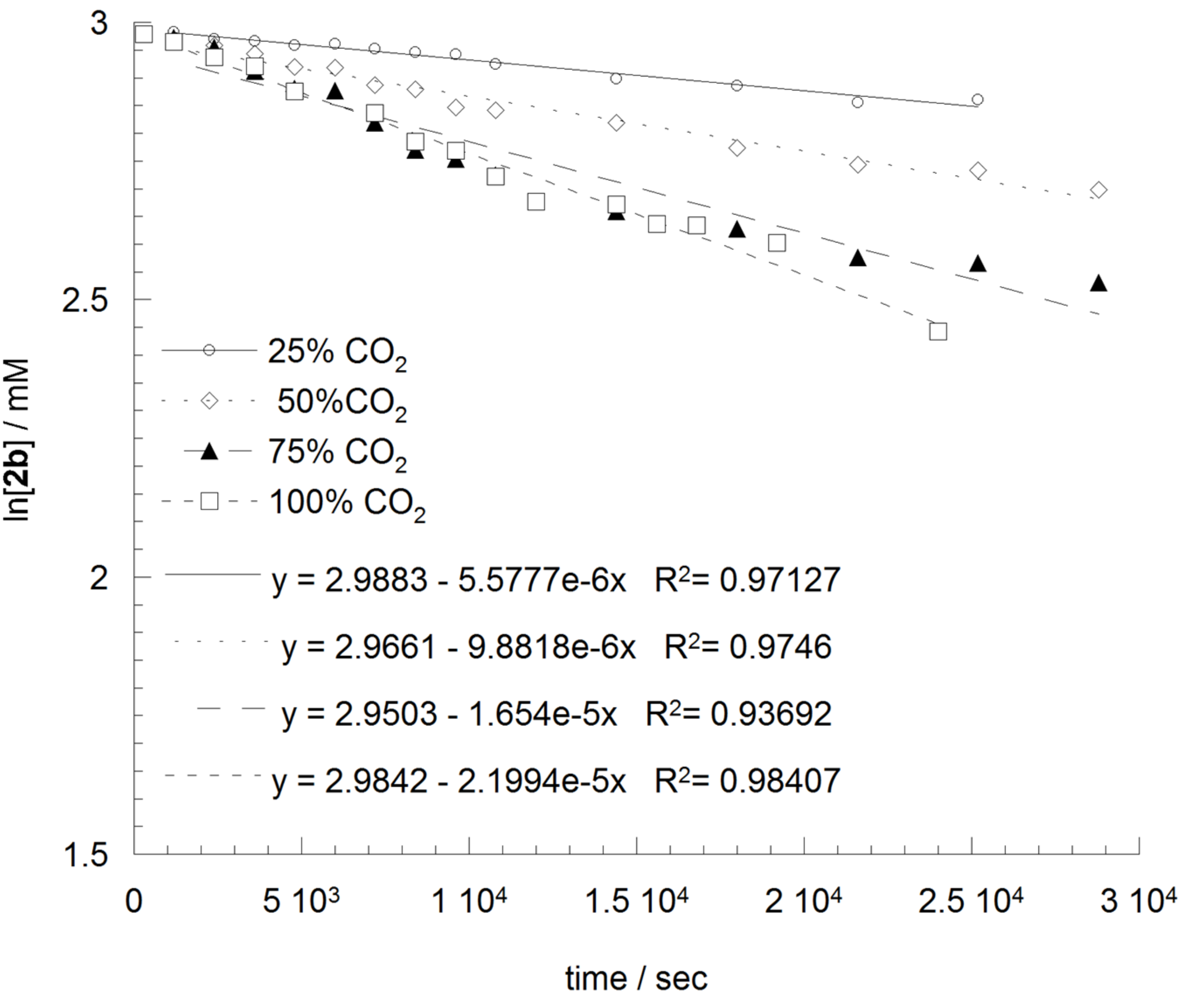
(3) $k_{obs} = k_2[CO_2]$

(4) $v = k_{obs}[\mathbf{2b}]$

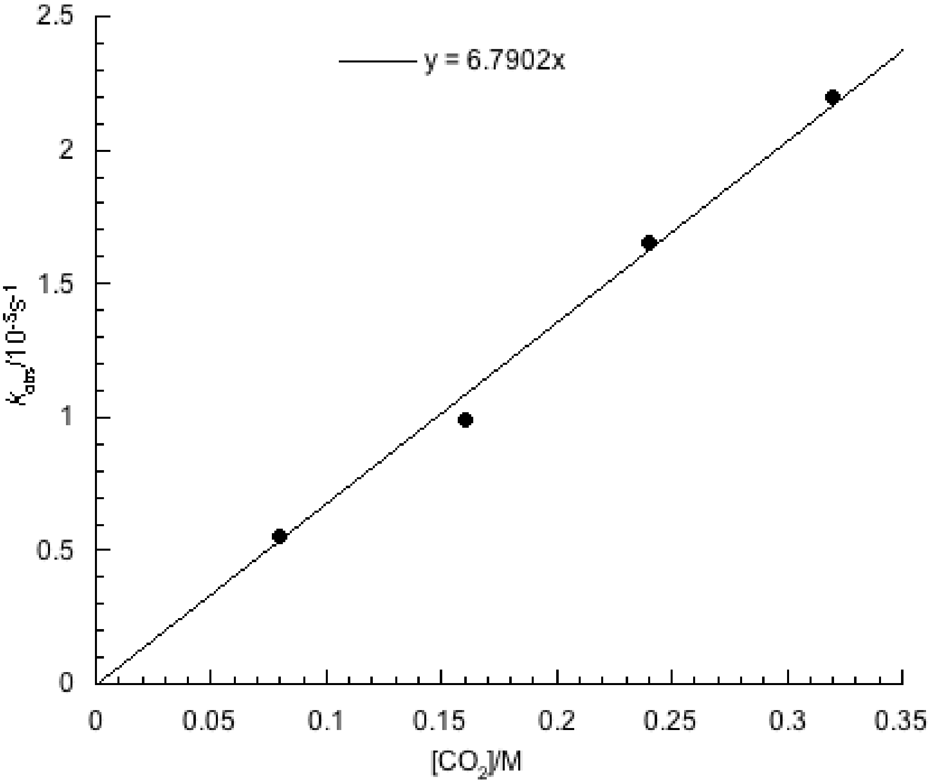
SFigure 8. Plots of reaction rate versus time at three different starting **2b** concentrations, 25°C temperature, 1 bar CO_2 pressure,10 mL acetonitrile. The slope is 10^{-7} k_{obs}.



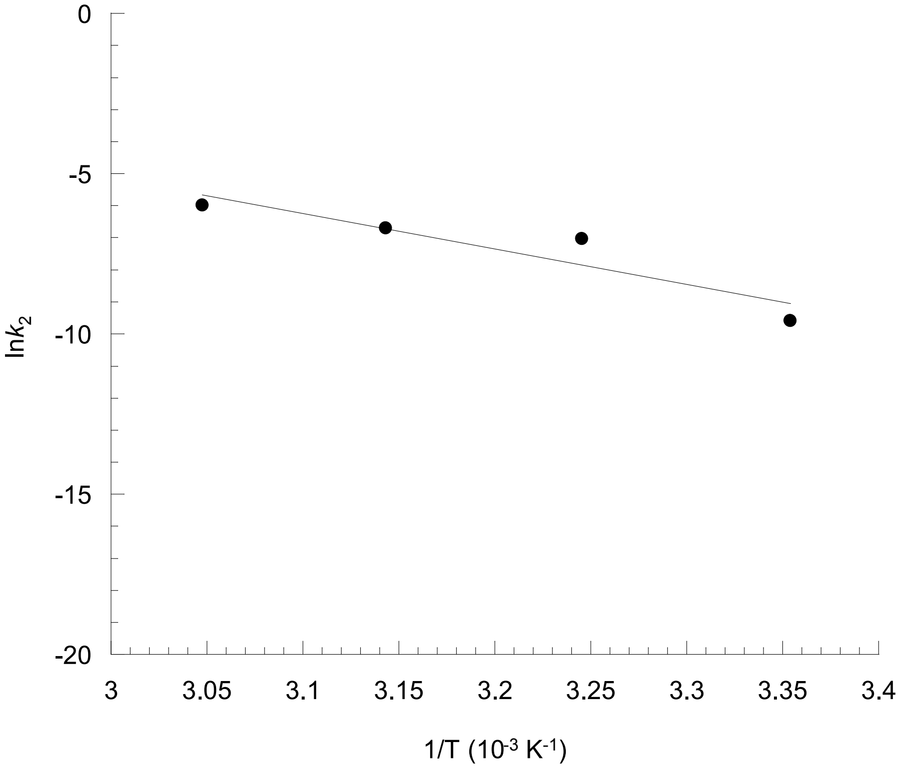
SFigure 9. Plots of ln [**2b**] versus time at various CO_2 partial pressures. Open circles pCO_2= 0.25 bar, open diamonds pCO_2 = 0.50 bar, filled triangles pCO_2 = 0.75 bar, open squares pCO_2 = 1 bar. All reactions were carried out at 25°C in the presence of excess of Ar-CO_2 gas mixtures in 10 mL acetonitrile.



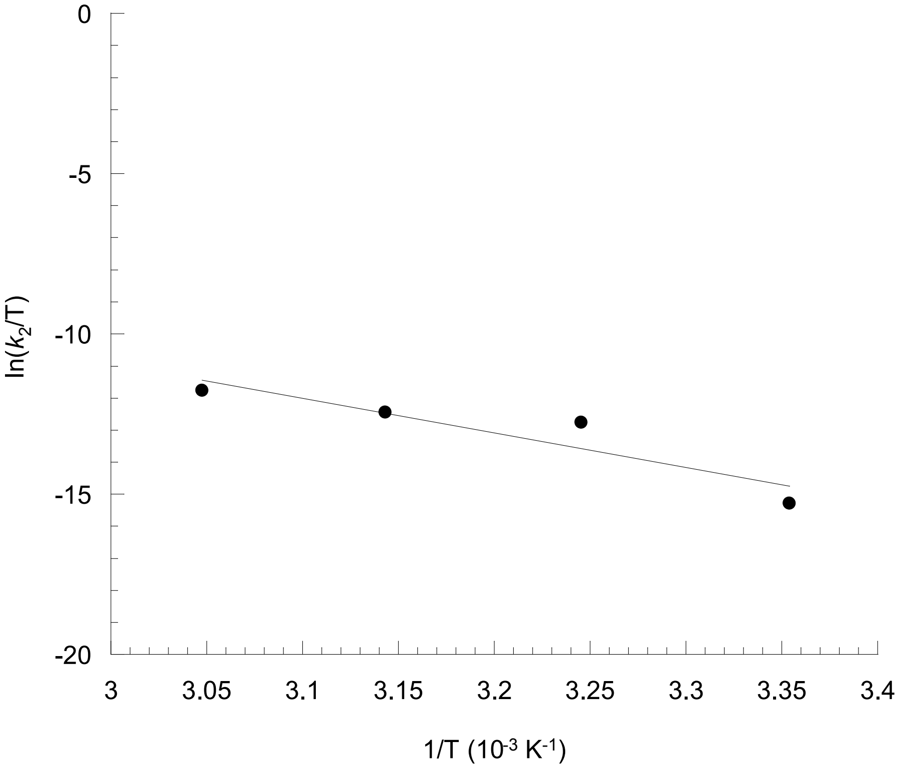
SFigure 10. Plots of the versus the CO_2 concentration. 25°C, 1 bar CO_2 pressure, 10 mL acetonitrile.The slope is $10^{-5}k_2$, [**2b**] = $2x10^{-2}$ M.



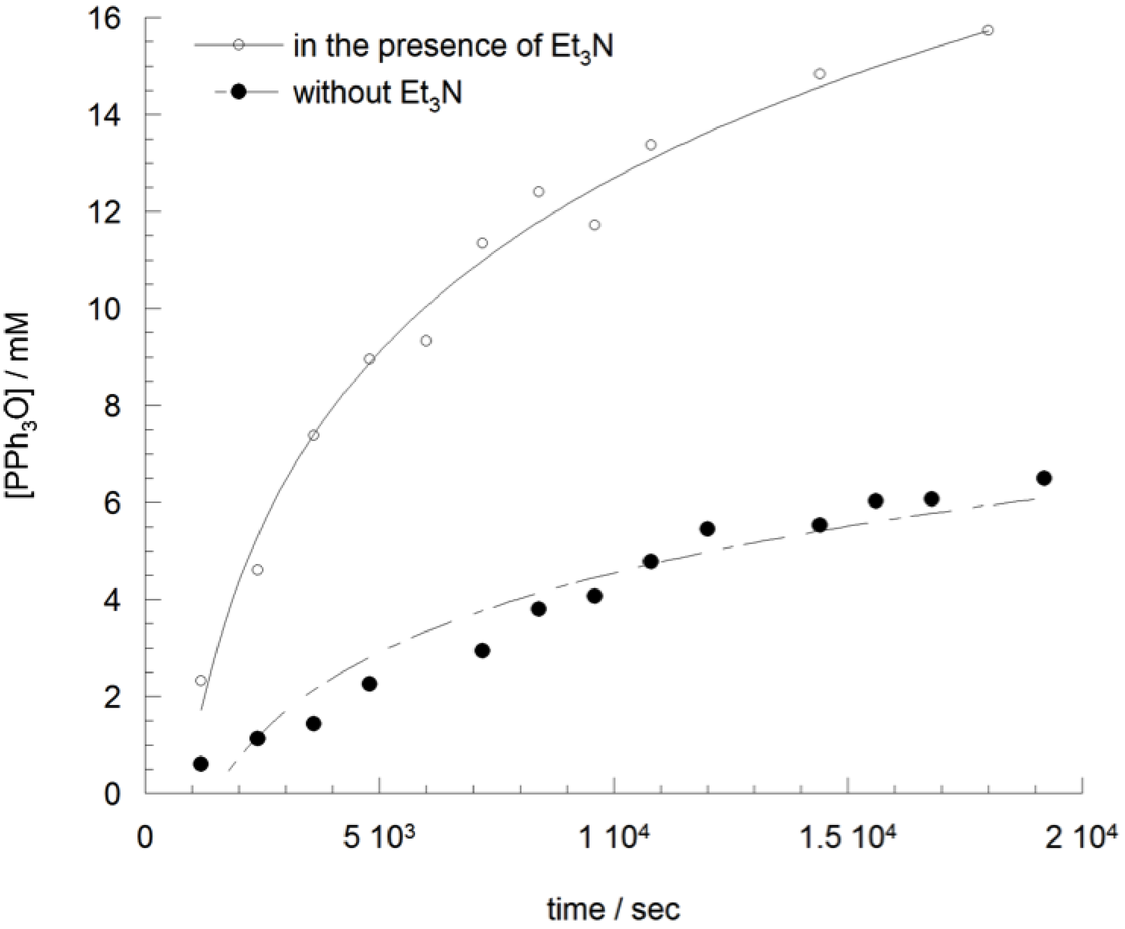
SFigure 11. The Arrhenius plot. Measurements were carried out at four different temperatures: 25, 35, 45, 55°C. [**2b**] = 20 mM, 1 bar CO_2 pressure, 10 mL acetonitrile.



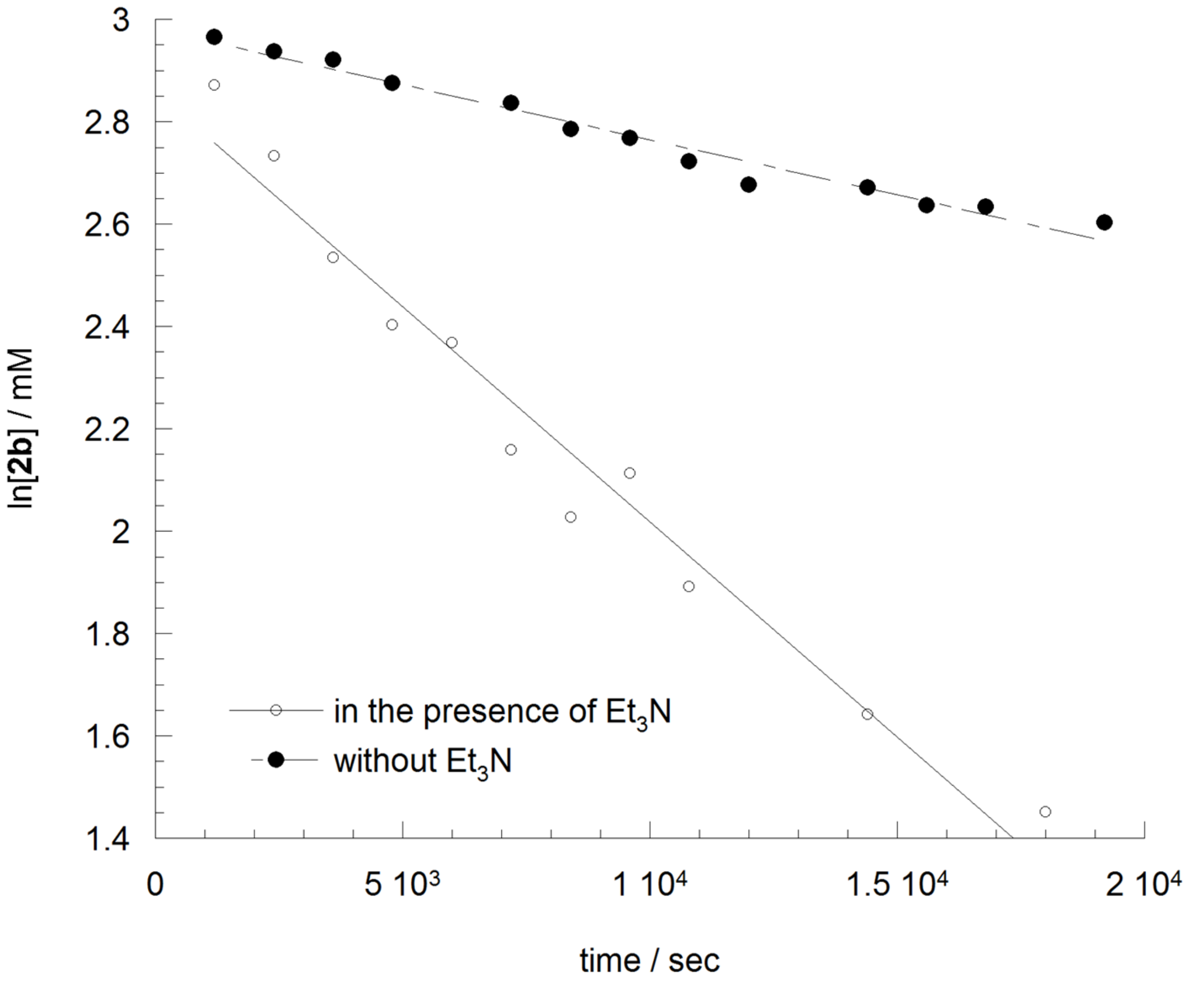
SFigure 12. The Eyring plot. Measurements were carried out at four different temperatures: 25, 35, 45, 55°C. [**2b**] = 20 mM, 1 bar CO_2 pressure, 10 mL acetonitrile.



SFigure 13. Effect of added Et_3N (1 equivalent) on the reaction rate. **2b** = 20 mM in 10 mL CH_3CN solution under 1 bar CO_2 at 25°C.



SFigure 14. ln [**2b**] versus time. Effect of added Et_3N on the reaction rate in 10 mL CH_3CN solution with concentration of 20 mM **2b** under 1 bar CO_2 at 25°C.
$k_2 = 6.87 \times 10^{-5}$ $M^{-1}s^{-1}$, $k_2^{Et3N} = 2.87 \times 10^{-4}$ $M^{-1}s^{-1}$.



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STable 1. Summary of the kinetic data.

No.	T (K)	$10^2[CO_2]^*$ (M)	10^2[**2b**] (M)	$10^5\, k_2$ / $M^{-1}s^{-1}$	$10^5\, k_{obs}$ / s^{-1}	$10^7\, v$ / Ms^{-1}
1	298	32	1	7.08±0.28	2.26±0.09	2.26±0.09
2	298	32	2	6.87±0.25	2.20±0.08	4.40±0.16
3	298	32	4	6.89±0.26	2.21±0.08	8.82±0.33
4	298	24	2	6.89±0.65	1.65±0.16	3.31±0.31
5	298	16	2	6.18±0.30	0.99±0.05	1.98±0.10
6	298	8	2	6.98±0.36	0.56±0.03	1.12±0.06
**				**6.81±0.12**		
7	308	25	2	90.56±2.05	22.64±0.51	45.28±1.03
8	318	20	2	124.9±7.71	24.97±1.54	49.94±3.08
9	328	16	2	254.6±27.50	40.48±4.40	80.96±8.80
Et_3N	298	32	2	28.69±2.42	91.80±0.78	18.36±1.55

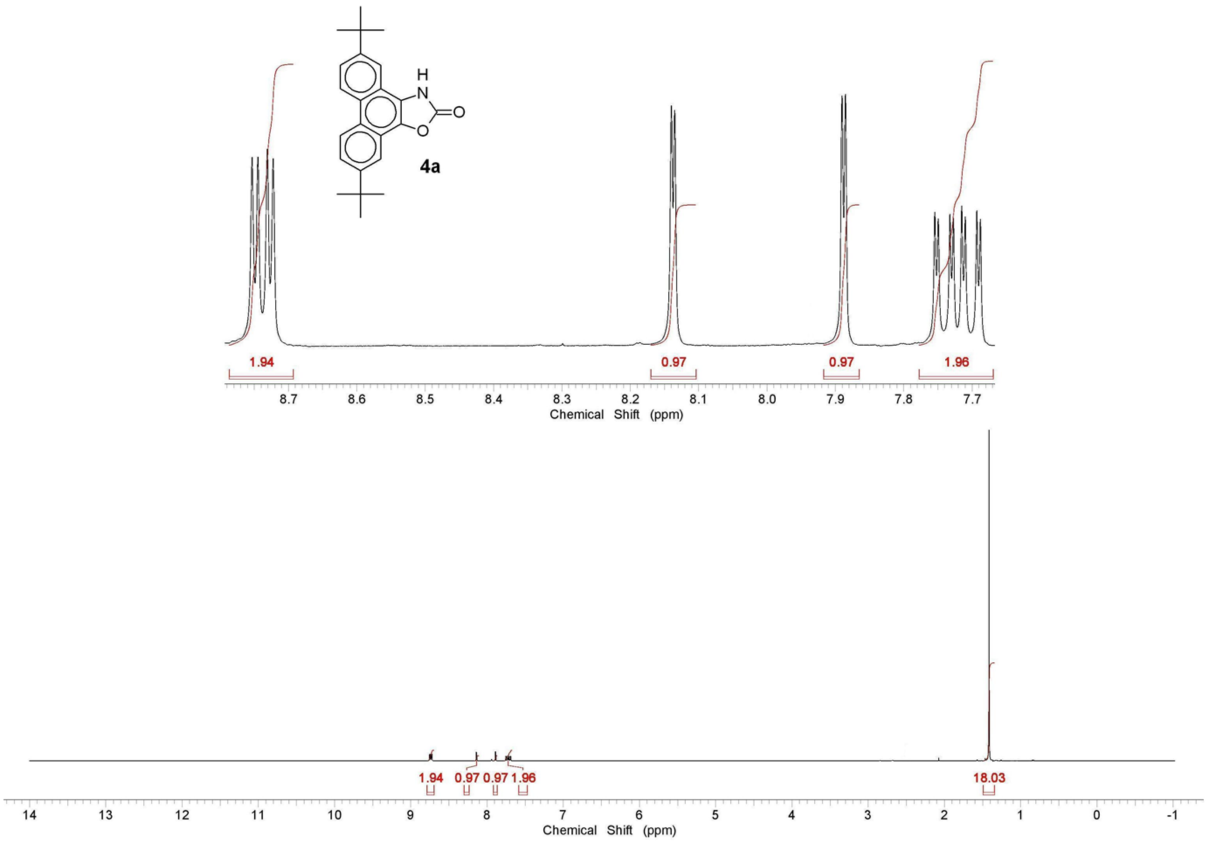
**Mean value of the kinetic constant k_2 and its standard deviations $\sigma(k_2)$ were calculated as $k_2 = (\sum_i w_i k_i/\sum_i w_i)$ and $\sigma(k_2) = (\sum_i w_i(k_i-k_2)^2/(n-1)\sum_i w_i)^{1/2}$, where $w_i = 1/\sigma^2_i$.

*CO_2 solubility data from the paper: A. Gennaro, A. A. Isse, E. Vianello, *J. Electroanal. Chem*. **1990**, *289,* 203-215

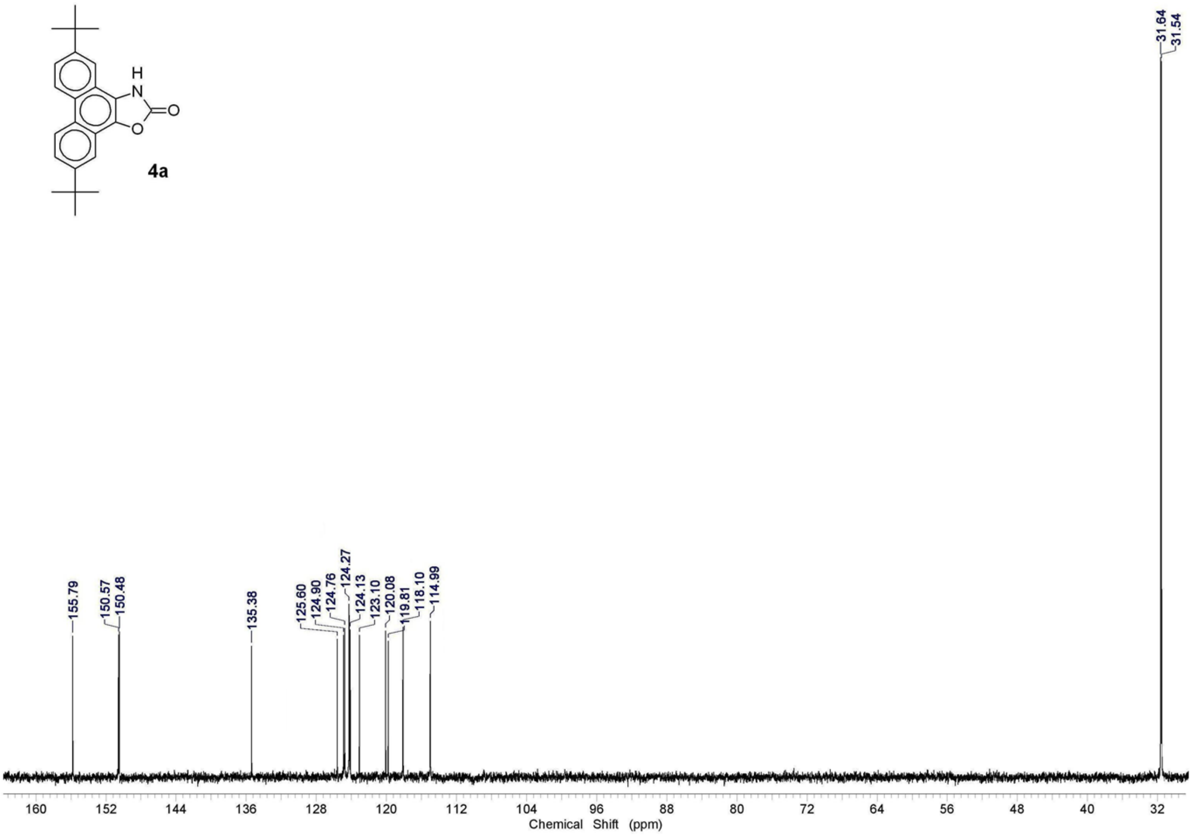
STable 3. Summary of the activation parameters.

E_a kJ/mol	$\Delta H^‡$ kJ/mol	$\Delta S^‡$ J/molK
91.8±26.5	89.2±26.6	-21±10

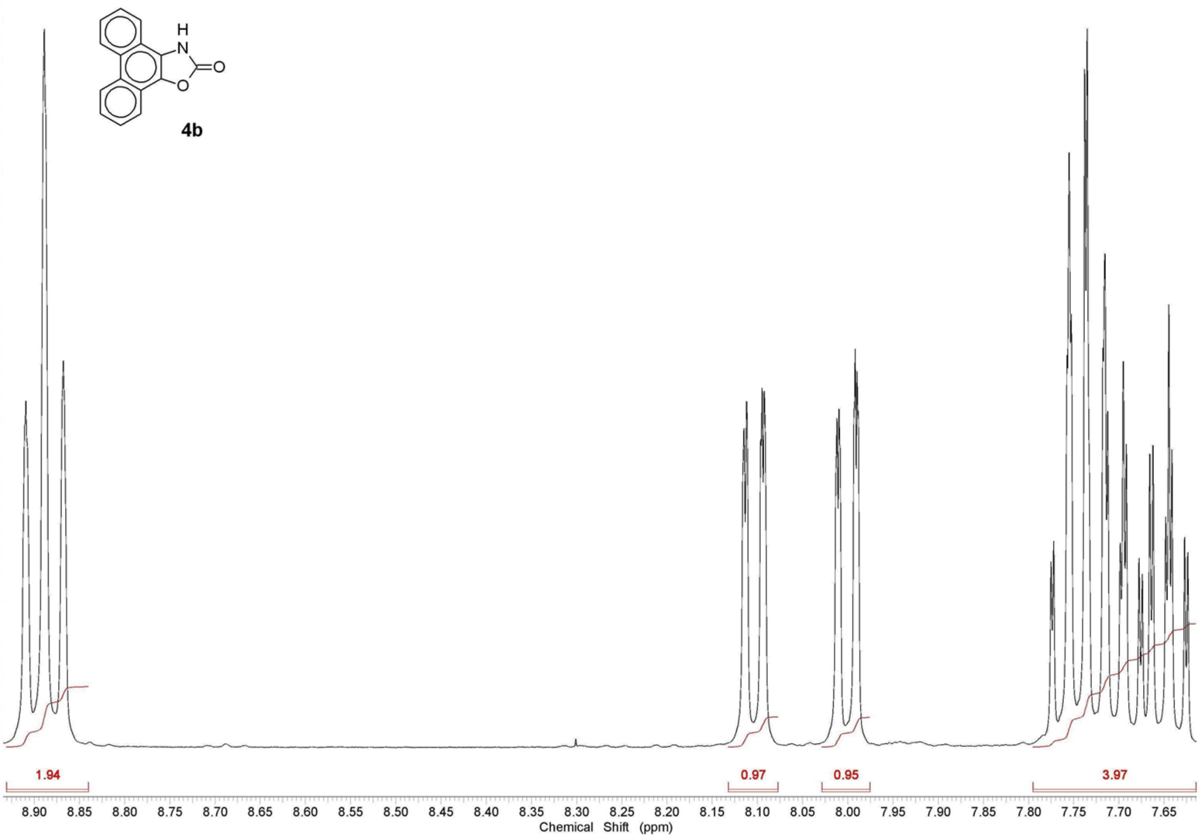
SFigure 15. The ^{1}H NMR spectrum of **4a**.



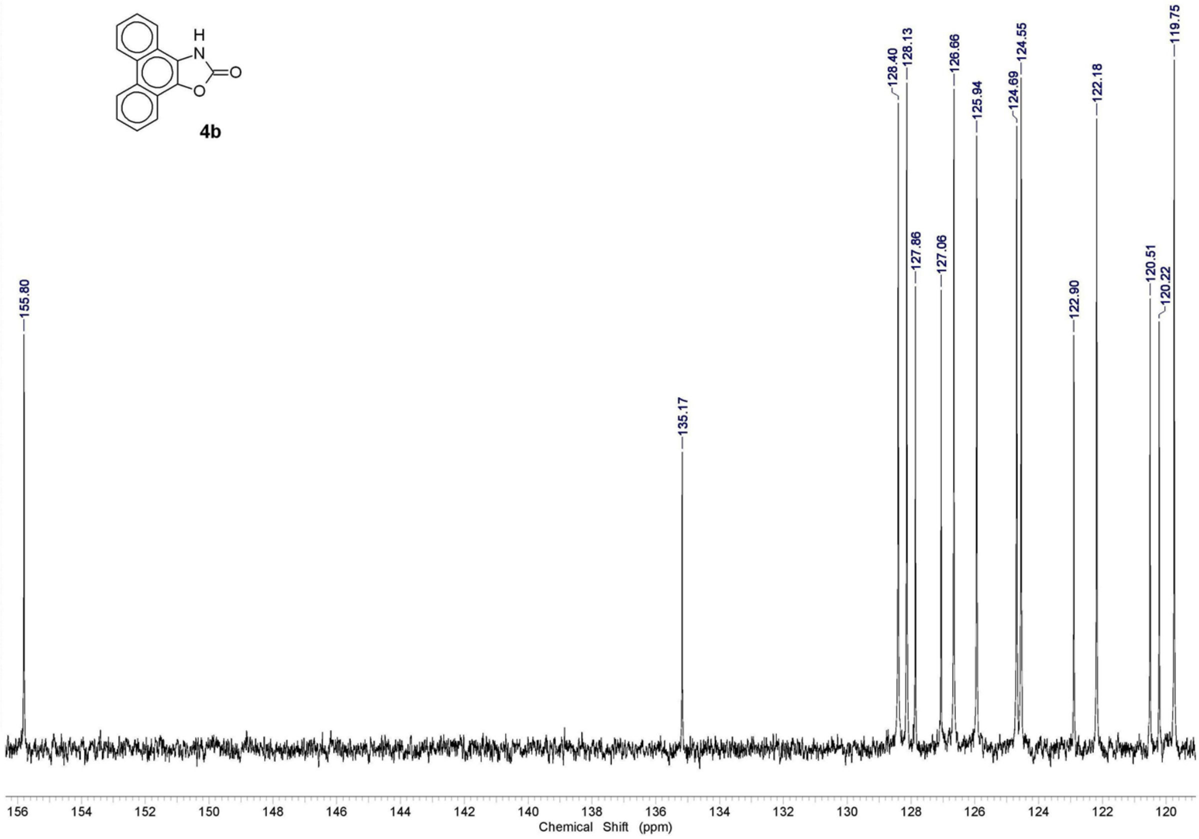
SFigure 16. The ^{13}C NMR spectrum of **4a**.



SFigure 17. The ^{1}H NMR spectrum of **4b.**

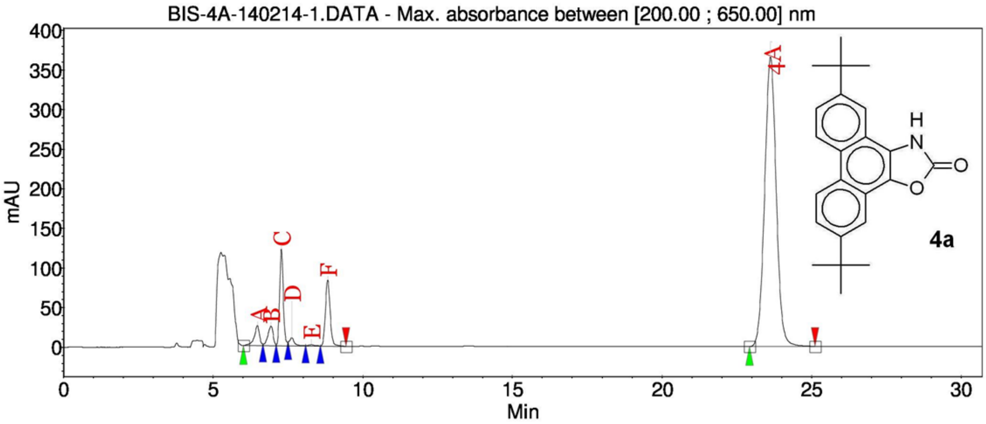


SFigure 18. The ^{13}C NMR spectrum of **4b.**



SFigure 19. The HPLC chromatogram of **4a.**

BIS-4A-140214-1 2/14/2014 7:39:38 PM kval-ap-130409-5

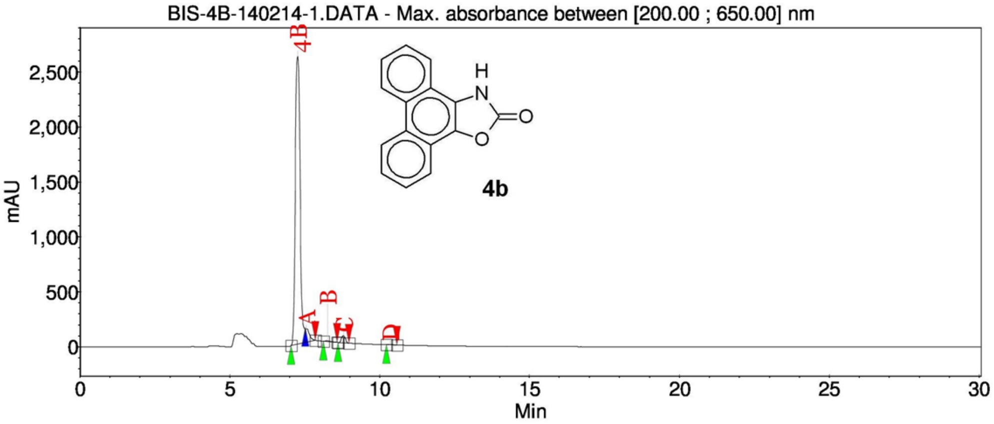


Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	A	6.480	2.50	25.4	5.2	2.501
2	B	6.933	2.41	25.1	5.0	2.414
3	C	7.279	8.27	122.0	17.3	8.275
4	D	7.626	1.01	10.4	2.1	1.008
5	E	8.279	0.23	1.7	0.5	0.227
6	F	8.826	7.37	83.2	15.4	7.369
7	4A	23.625	78.21	365.3	163.5	78.206
Total			100.00	633.1	209.0	100.000

No PDA 2D View in this channel.

SFigure 20. The HPLC chromatogram of **4b.**

BIS-4B-140214-1 2/14/2014 8:12:18 PM kval-ap-130409-5



Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	4B	7.266	94.21	2616.7	483.1	94.213
5	A	7.546	3.57	122.5	18.3	3.573
2	B	8.253	0.20	6.2	1.0	0.199
3	C	8.786	1.90	66.1	9.7	1.900
4	D	10.346	0.12	4.0	0.6	0.116
Total			100.00	2815.4	512.7	100.000

No PDA 2D View in this channel.