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Amberlyst-15 as a highly efficient and regenerative catalyst in the one-pot synthesis of areno[*d*][1,2]oxaphospholes

Makar A. Zaborsky, Dmitry A. Tatarinov, Rezeda M. Salakhova, Eliza E. Baynazarova, Olga B. Babaeva, Khasan R. Khayarov and Vladimir F. Mironov

Content

General information

Commercially available reagents were used. Commercially available solvents were purified by standard procedures. All reactions were carried out in the air**.** The target products were stored in closed flasks in an argon atmosphere. Flash column chromatography was performed using silica gel (230-400 mesh).

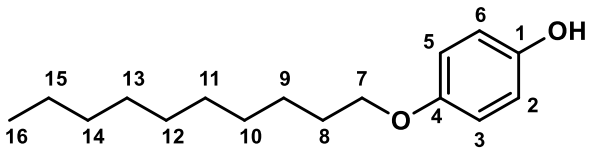
NMR experiments were carried out on Bruker Avance-400 MHz [400 MHz (^{1}H), 101 MHz (^{13}C), 162 MHz (^{31}P)], Bruker Avance-600 MHz [242.9 MHz (^{31}P)] spectrometers. Chemical shifts are reported on the δ (ppm) scale using the signals of the residual protons or carbon nuclei of $CDCl_3$ as the internal standard and H_3PO_4 as the external standard (^{31}P). Coupling constants (*J*) are reported in Hertz and refer to apparent peak multiplications. The abbreviations s, ws, d, t, q, and m stand for singlet, wide singlet, doublet, triplet, quartet, and multiplet in that order. The high resolution mass spectra (HRMS) with electrospray ionization (ESI) were obtained on ESI-QTOF Impact II mass spectrometer with Elute UHPLC system (Bruker Daltonik GmbH, Germany) in the positive or negative mode in the mass range of 50–1900. IR spectra were recorded for thin film between KBr plates on a Bruker Tensor 27 spectrometer.

General procedure for synthesis of arenooxaphospholenes 7a-f using Amberlyst-15

α-Hydroxy phosphonate (1.825 mmol) and the corresponding *para*-substituted phenol (1.825 mmol), as well as Amberlyst-15 in an amount of 30 % by weight, were placed in a 50 mL round-bottomed flask. The mixture was heated by stirring in the open air at a temperature of 140 °C for 3 hours. The resulting thick mass was refluxed in 1,2-dichloroethane, 300 mol% triethyl orthoformate was added, and the solution was refluxed with a reflux condenser while stirring for 3 hours. Then, gradient flash chromatography was performed on a dry column to isolate the desired reaction product. First, a mixture of eluents (hexane and ethyl acetate 4 : 1) was used to separate unreacted phenol and nonpolar impurities, then ethyl acetate was used to separate the product. Since the cyclic product partially or completely opened (hydrolyzed) and/or dealkylated after chromatography, the mixture obtained after purification was dissolved in 3 ml of *o*-xylene, 300 mol% triethyl orthoformate was added and the solution was refluxed with a reflux condenser for 12-17 hours. In the case of a poor dissolution of substances in *o*-xylene, 1,2-dichloroethane or 1,2-dimethoxyethane (about 1/10 of the volume of *o*-xylene) was used as a co-solvent and the mixture was refluxed in a chemical reactor at 140 °C and increased pressure for the same time. When the cyclization and re-alkylation were complete, the solvent was evaporated on a rotary evaporator, the resulting products were dried from solvent and triethyl orthoformate residues at 100 °C and evacuated with an oil pump (0.05-0.07 Torr) for 30 minutes. To prevent the hydrolysis and dealkylation, the substances were stored in closed flasks in an argon atmosphere. All solvents used in this method were dried.

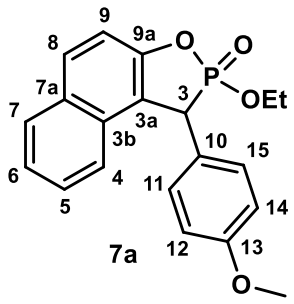
Synthesis of 4-decyloxyphenol

The method, described earlier, was used with some modifications.[S1] Sodium methoxide (0.108 g, 2 mmol) in 5 mL of methanol were added dropwise to a solution of hydroquinone (0.22 g, 2 mmol) in 5 mL of methanol and the resulting solution was mixed for 10 minutes. After that, the solvents were evaporated dry on a rotary evaporator. The solid residue was cooled to the room temperature, and l-bromodecane (0.42 mL, 2 mmol) in 3 mL of dry dimethylformamide was added. The resulting mixture was stirred for 3 hours at 110 °C in an argon atmosphere. The brown solution was then cooled and diluted with 500 mL of cold water. The product was filtered and dried at room temperature in vacuum. Next, the mixture was subjected to flash chromatography on a dry carrier (petroleum ether/ethyl acetate = 10/l) as an eluent). The fractions with the product were collected in a separate flask. After evaporation of the solvent, the target 4-decyloxyphenol was obtained as a white solid.



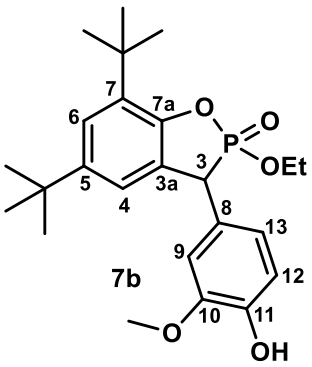
4-Decyloxyphenol, white solid (47 %, 0.235 g). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ ppm, *J* Hz: 6.82-6.74 (m, 4H, H^{Ar}), 3.91 (t, $^{3}J_{HH}$ 6.6, 2H, H^{7}), 3.42 (s, 1H, OH), 1.82-1.71 (m, 2H, H^{8}), 1.50-1.40 (m, 2H, H^{15}), 1.29 (s, 12H, $H^{9–14}$), 0.90 (t, $^{3}J_{HH}$ 6.9, 3H, H^{16}). The data are consistent with reported values.[S2]

Characterization of arenooxaphospholes 7a-f



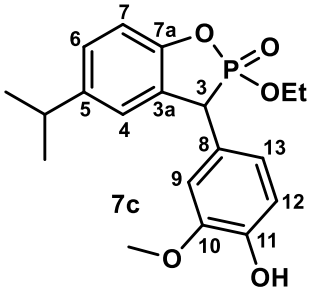
2-Ethoxy-3-(4-methoxyphenyl)-3*H*-naphtho[*d*][1,2]oxaphosphole 2-oxide (7a). A mixture of two diastereoisomers d_1 and d_2, 3 : 2 respectively. Yellow-orange oil (73 %, 0.236 g). Found (%):C, 66.47; H, 7.82; P, 7.24. $C_{20}H_{19}O_4P$. Calculated (%): C, 66.65; H, 7.69; P, 7.16. IR spectrum, ν (cm^{-1}): 3399, 3063, 2931, 2839, 2249, 1891, 1657, 1612, 1512, 1461, 1376, 1348, 1300, 1251, 1180, 1153, 1112, 1033, 966, 911, 865, 834, 815, 742, 649, 563, 514, 470, 428. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ ppm, *J* Hz: 7.86, 7.85 and 7.83 (three br. d, $^{3}J_{HH}$ 9.5, 8.7 and 8.7, 2H, H^{8}, H^{7}, d_1–d_4), 7.36 and 7.32 (two br. d, $^{3}J_{HH}$ 9.3 and 9.3, 2H, H^{4}, H^{9}, d_1–d_4), 7.27-7.30 and 7.33-7.37 (two m, 2H, H^{5}, H^{6}, d_1–d_4), 7.10 and 7.06 (br. dd and dd, $^{3}J_{HH}$ 8.5, $^{4}J_{PH}$ 2.4 and $^{3}J_{HH}$ 8.8, $^{4}J_{PH}$ 2.7, 2H, $H^{11,15}$,

d_1–d_4), 6.85 and 6.83 (two br. d, $^3J_{HH}$ 8.5 and 8.7, 2H, $H^{12,14}$, d_1–d_4), 4.95 and 4.75 (two br. d, $^2J_{PH}$ 20.2 and 19.5, 1H, PCH, d_1/d_2 and d_3/d_4), 4.30-4.41 and 4.0-4.13 (two m, 2H, OCH_2, d_3/d_4 and d_1/d_2), 3.78 and 3.74 (two s, 3H, OCH_3, d_1/d_2 and d_3/d_4), 1.40 and 1.02 (two t, $^3J_{HH}$ 7.1 and 7.1, 3H, CH_3, d_3/d_4 and d_1/d_2). ^{13}C-{^1H} NMR spectrum (101 MHz, $CDCl_3$) δ_C ppm, *J* Hz: 159.09 (br. s, C^{13}, d_1/d_2), 159.06 (br. s, C^{13}, d_3/d_4), 150.95 (d, $^2J_{PC}$ 13.0, C^{9a}, d_1/d_2), 150.69 (d, $^2J_{PC}$ 11.7, C^{9a}, d_3/d_4), 130.86 (br. s, C^8, d_1–d_4), 130.75 (br. s, C^{7a}, d_1/d_2), 130.65 (br. s, C^{7a}, d_3/d_4), 130.78 (d, $^3J_{PC}$ 15.6, C^{3b}, d_1/d_2), 130.70 (d, $^3J_{PC}$ 15.9, C^{3b}, d_3/d_4), 129.67 (d, $^3J_{PC}$ 5.3, $C^{11,15}$, d_1/d_2), 129.50 (d, $^3J_{PC}$ 5.8, $C^{11,15}$, d_3/d_4), 129.12 and 129. 10 (two br. s, C^7, d_1–d_4), 127.57 and 127.33 (two br. s, C^5, d_1–d_4), 126.37 (d, $^2J_{PC}$ 9.1, C^{10}, d_1/d_2), 125.96 (d, $^2J_{PC}$ 6.5, C^{10}, d_3/d_4), 124.76 (br. s, C^6, d_3/d_4), 124.65 (br. s, C^6, d_1/d_2), 123.78 (br. s, C^4, d_1/d_2), 123.55 (br. s, C^4, d_3/d_4), 119.94 (d, $^3J_{PC}$ 8.1, C^{3a}, d_3/d_4), 118.86 (d, $^3J_{PC}$ 8.4, C^{3a}, d_1/d_2), 114.65 (d, $^4J_{PC}$ 2.9, $C^{12,14}$, d_3/d_4), 114.40 (d, $^4J_{PC}$ 3.0, $C^{12,14}$, d_1/d_2), 114.15, 114.11, 114.10 and 114.06 (four d, $^3J_{PC}$ 11.6, 11.9, 10.9 and 10.5, C^9, d_1–d_4), 64.68 and 64.62 (two d, $^2J_{PC}$ 5.9 and 6.6, O**C**H_2, d_3/d_4), 64.66 and 63.64 (two d, $^2J_{PC}$ 6.6 and 7.6, O**C**H_2, d_1/d_2), 55.30 and 55.23 (two s, O**C**H_3, d_1–d_4), 42.81 and 42.76 (two d, $^1J_{PC}$ 117.8 and 116.7, C^3, d_1/d_2), 41.42 and 41.35 (two d, $^1J_{PC}$ 121.2 and 120.8, C^3, d_3/d_4), 16.56 and 16.52 (two d, $^3J_{PC}$ 5.1 and 6.4, CH_3, d_3, d_4), 16.07 (d, $^3J_{PC}$ 5.1, CH_3, d_1/d_2). ^{31}P-{^1H} NMR (243 MHz, $CDCl_3$) δ_P, ppm: 45.0 and 42.5 (two br. s, d_1–d_4). ^{31}P-{^1H} NMR spectrum (243 M, $CDCl_3$) δ_P: 45.0 and 42.5 (two br. s, d_1–d_4).



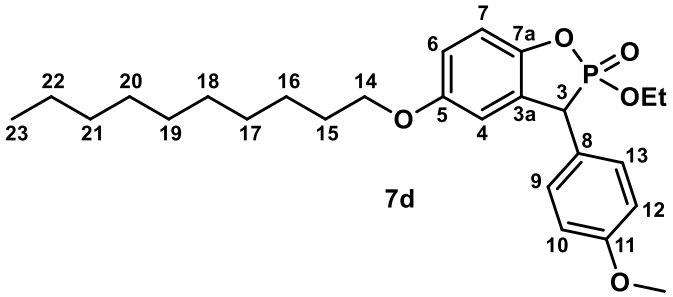
5,7-Di-*tert*-butyl-2-ethoxy-3-(4-hydroxy-3-methoxyphenyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (7b). A mixture of four diastereoisomers d_1/d_2 and d_3/d_4 with the ratio of 3 : 2 was obtained as yellow-orange oil (95 %, 0.375 g). Found (%): C, 67.91; H, 5.77; P, 8.63. $C_{24}H_{33}O_5P$. Calculated (%): C, 67.79; H, 5.40; P, 8.74. IR spectrum, ν (cm^{-1}): 3324, 2961, 2910, 2871, 2248, 1602, 1516, 1462, 1393, 1365, 1269, 1211, 1156, 1127, 1100, 1036, 973, 914, 867, 811, 735, 647, 615, 590, 555, 535, 468, 440. ^1H NMR spectrum (400 MHz, $CDCl_3$) δ ppm, *J* Hz: 7.30 and 7.29 (two br. d, $^4J_{HH}$ 2.4 and 2.3, 1H, H^6, d_1–d_4), 6.99 (ddd, $^4J_{HH}$ 2.4, $^4J_{HH}$ 1.1, $^4J_{PH}$ 1.1, 1H, H^4, d_3/d_4), 6.97 (ddd, $^4J_{HH}$ 2.3, $^4J_{HH}$ 1.1, $^4J_{PH}$ 1.1, 1H, H^4, d_1/d_2), 6.90 (br. d, $^3J_{HH}$ 8.0, 1H, H^{12}, d_1/d_2), 6.81 (br. d, $^3J_{HH}$ 7.9, 1H, H^{12}, d_3/d_4), 6.78 (d, $^4J_{HH}$ 2.2, 1H, H^9, d_1/d_2), 6.76 (ddd, $^3J_{HH}$ 8.0, $^4J_{PH}$ 2.8, $^4J_{HH}$ 2.2, 1H, H^{13}, d_1/d_2), 6.62 (d, $^4J_{HH}$ 2.2, 1H, H^9, d_3/d_4), 6.61 (ddd, $^3J_{HH}$ 7.9, $^4J_{PH}$ 2.6, $^4J_{HH}$ 2.2, 1H, H^{13}, d_3/d_4), 6.31 (very br. s, 2H, OH, d_1–d_4), 4.57 (br. d, $^2J_{PH}$ 19.3, 1H, PCH, d_1/d_2), 4.33 (br. d, $^2J_{PH}$ 20.0, 1H, PCH, d_3/d_4), 4.28-4.38 (m, 2H, $^3J_{PH}$ 9.7 . $^3J_{HH}$ 7.1, OCH_2, d_3/d_4), 3.98-4.07 (m, 2H, $^3J_{PH}$ 10.0 . $^3J_{HH}$ 7.1,

OCH_2, d_1/d_2), 3.82 (s, 3H, $C^{10}OCH_3$, d_1/d_2), 3.76 (s, 3H, $C^{10}OCH_3$, d_3/d_4), 1.45 and 1.44 (two s, 9H, $C^5C(CH_3)_3$, d_3/d_4 and d_1/d_2), 1.42 (t, $^3J_{HH}$ 7.1, 3H, CH_3, d_3/d_4), 1.27 and 1.26 (two s, 9H, $C^5C(CH_3)_3$, d_1/d_2 and d_3/d_4), 1.03 (br. t, $^3J_{HH}$ 7.1, 3H, CH_3, d_1/d_2). ^{13}C-{^1H} NMR spectrum (101 MHz, $CDCl_3$) δ_C ppm, *J* Hz: 148.97 (d, $^2J_{PC}$ 10.7, C^{7a}, d_1/d_2), 148.63 (d, $^2J_{PC}$ 11.0, C^{7a}, d_3/d_4), 147.14 (d, $^4J_{PC}$ 2.5, C^{10}, d_3/d_4), 147.01 (d, $^4J_{PC}$ 2.8, C^{10}, d_1/d_2), 146.33 (s, C^5, d_3/d_4), 146.14 (s, C^5, d_1/d_2), 145.44 (d, $^5J_{PC}$ 2.8, C^{11}, d_3/d_4), 145.40 (d, $^5J_{PC}$ 3.5, C^{11}, d_1/d_2), 134.91 (d, $^3J_{PC}$ 9.0, C^7, d_3/d_4), 134.77 (d, $^3J_{PC}$ 8.9, C^7, d_1/d_2), 127.57 (d, $^2J_{PC}$ 6.1, C^{3a}, d_3/d_4), 127.17 (d, $^2J_{PC}$ 5.8, C^{3a}, d_1/d_2), 126.03 (d, $^2J_{PC}$ 6.8, C^8, d_3/d_4), 124.90 (d, $^2J_{PC}$ 9.8, C^8, d_1/d_2), 123.64 and 123.57 (two s, C^6, d_3/d_4), 123.56 and 123.29 (two s, C^6, d_1/d_2), 122.16 (d, $^3J_{PC}$ 6.0, C^{13}, d_1/d_2), 122.10 (d, $^3J_{PC}$ 16.3, C^4, d_3/d_4), 121.78 (d, $^3J_{PC}$ 6.2, C^{13}, d_3/d_4), 121.74 (d, $^3J_{PC}$ 15.3, C^4, d_1/d_2), 114.97 (d, $^4J_{PC}$ 2.9, C^{12}, d_3/d_4), 114.90 (d, $^4J_{PC}$ 3.4, C^{12}, d_1/d_2), 111.81 (d, $^3J_{PC}$ 5.5, C^9, d_1/d_2), 111.38 (d, $^3J_{PC}$ 5.6, C^9, d_3/d_4), 64.15 and 63.58 (two d, $^2J_{PC}$ 6.7 and 7.5, CH_2, d_1/d_2), 64.17 and 64.11 (two d, $^2J_{PC}$ 5.3 and 7.5, CH_2, d_3/d_4), 56.03 and 55.88 (two s, OCH_3, d_1/d_2), 55.85 and 55.81 (two s, OCH_3, d_3/d_4), 43.75 and 42.67 (two d, $^1J_{PC}$ 119.1 and 119.7, C^3, d_1/d_2), 41.94 and 41.88 (two d, $^1J_{PC}$ 121.6 and 121.7, C^3, d_3/d_4), 34.78 (s, C^5–**C**, d_1/d_2), 34.75 (s, C^5–**C**, d_3/d_4), 34.66 (s, C^7–**C**, d_3/d_4), 34.63 (s, C^7–**C**, d_1/d_2), 31.58 (s, C^5–C(**C**$H_3)_3$, d_3/d_4), 31.53 (s, C^5–C(**C**$H_3)_3$, d_1/d_2), 29.55 (s, C^7–C(**C**$H_3)_3$, d_3/d_4), 29.50 (s, C^7–C(**C**$H_3)_3$, d_1/d_2), 16.66 and 16.60 (two d, $^3J_{PC}$ 5.8 and 5.7, CH_3, d_3/d_4), 16.20 and 16.18 (two d, CH_3, $^3J_{PC}$ 5.6 and 5.6, d_1/d_2). ^{31}P-{^1H} NMR spectrum (162 MHz, $CDCl_3$) δ_P ppm: 44.4 and 43.4 (two br. s, d_1–d_4).



2-Ethoxy-3-(4-hydroxy-3-methoxyphenyl)-5-isopropyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (7c). A mixture of four diastereoisomers d_1/d_2 and d_3/d_4 with the ratio of 1 : 1 was obtained as yellow oil (86 %, 0.284 g). Found (%): C, 63.27; H, 6.65; P, 8.33. $C_{19}H_{23}O_5P$. Calculated (%): C, 62.98; H, 6.40; P, 8.55. IR spectrum, ν (cm^{-1}): 3259, 2933, 2250, 1727, 1606, 1515, 1486, 1464, 1197, 1095, 912, 731, 647, 621, 495. ^1H NMR spectrum (400 MHz, $CDCl_3$) δ ppm, *J* Hz: 7.18 and 7.10 (two m, $^3J_{HH}$ 8.8, $^4J_{HH}$ 2.6 and $^3J_{HH}$ 8.8, $^4J_{HH}$ 2.6, 2H, $H^{9,13}$, d_1–d_4), 7.16 and 7.15 (two br. dd, $^3J_{HH}$ 8.4, $^4J_{HH}$ 2.6 and $^3J_{HH}$ 8.4, $^4J_{HH}$ 2.6, 1H, H^6, d_1–d_4), 7.01 and 7.0 (two br. d, $^3J_{HH}$ 8.4 and $^3J_{HH}$ 8.4, 1H, H^7, d_1–d_4), 6.96 and 6.94 (two br. m, $^4J_{HH}$ 2.5-2.6, $^4J_{HH}$ 1.1, $^4J_{PH}$ 1.1 and $^4J_{HH}$ 2.5-2.6, $^4J_{HH}$ 1.2, $^4J_{PH}$ 1.2, 1H, H^4, d_1–d_4), 6.91 and 6.88 (two m, $^3J_{HH}$ 8.8, $^5J_{PH}$ 0.8 and $^3J_{HH}$ 8.8, $^5J_{PH}$ 0.8, 2H, $H^{10,12}$, d_1–d_4), 4.60 and 4.39 (two br. d, $^2J_{PH}$ 20.8 and 19.2, 1H, PCH, d_1–d_4), 4.24-4.38 (two m, $^3J_{HH}$ 7.1, 2H, OCH_2, d_3/d_4), 4.02 and 3.99 (two dq, $^3J_{PH}$ 8.1, $^3J_{HH}$ 7.1 and $^3J_{PH}$ 8.1, $^3J_{HH}$ 7.1, 2H, OCH_2, d_1/d_2), 3.82 and 3.77 (two s, 3H, OCH_3, d_1–d_4), 2.84 and 2.83 (two sept, 1H, CH, d_1–d_4), 1.39 (t,

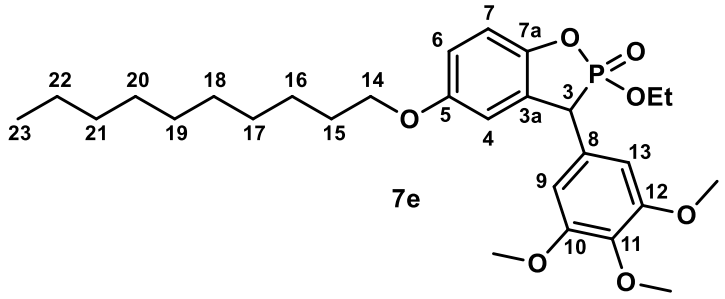
$^{3}J_{HH}$ 7.1, 3H, CH_3, d_3/d_4), 1.195, 1.192, 1.185 and 1.178 (four d, $^{3}J_{HH}$ 6.9, 6.9, 6.9 and 6.9, $^{3}J_{HH}$ 7.1, 6H, d_1–d_4), 1.0 (td, $^{3}J_{HH}$ 7.1, $^{4}J_{PH}$ 0.5, 3H, CH_3, d_1/d_2). ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) δ_C ppm, *J* Hz: 151.53 (d, $^{2}J_{PC}$ 11.7, C^{7a}, d_1), 150.55 (d, $^{2}J_{PC}$ 11.7, C^{7a}, d_2), 147.21 (d, $^{4}J_{PC}$ 2.8, C^{10}, d_2), 147.10 (d, $^{4}J_{PC}$ 2.0, C^{10}, d_1), 145.58 and 145.56 (two s, C^{11}, d_1/d_2), 144.65 (s, C^5, d_2), 144.58 (s, C^5, d_1), 127.74 and 126.93 (two d, $^{2}J_{PC}$ 6.2 and 6.6, C^{3a}, d_1/d_2), 127.42 and 127.27 (two s, C^6, d_1/d_2), 126.93 and 124.80 (two d, $^{2}J_{PC}$ 6.6 and 9.2, C^8, d_1/d_2), 125.33 and 124.99 (two d, $^{3}J_{PC}$ 16.3 and 15.7, C^4, d_2 and d_1), 121.96 and 121.88 (two d, $^{3}J_{PC}$ 8.0 and 8.2, C^{13}, d_1/d_2), 114.95 (br. s, C^{12}, d_1/d_2) 113.02 and 112.91 (two d, $^{3}J_{PC}$ 10.8 and 11.0, C^7, d_1/d_2), 111.71 and 111.43 (two d, $^{3}J_{PC}$ 5.3 and 5.8, C^9, d_1 and d_2), 64.32 (d, $^{2}J_{PC}$ 6.9, CH_2, d_1), 63.70 (d, $^{2}J_{PC}$ 7.4, CH_2, d_2), 55.92 (s, OCH_3, d_1), 55.77 (s, OCH_3, d_2), 43.63 (d, $^{1}J_{PC}$ 119.5, C^3, d_1), 43.61 (d, $^{1}J_{PC}$ 119.4, C^3, d_2), 42.86 (d, $^{1}J_{PC}$ 122.0, C^3, d_3), 42.84 (d, $^{1}J_{PC}$ 122.0, C^3, d_4), 33.73 (s, C^5–**C**H, d_1), 33.68 (s, C^5–**C**H, d_2), 24.15 and 24.0 (two s, CH(**C**H_3)$_2$, d_1), 24.156 and 24.08 (two s, CH(**C**H_3)$_2$, d_2), 16.45 (d, $^{3}J_{PC}$ 5.4, CH_3, d_2), 16.01 (d, $^{3}J_{PC}$ 5.6, CH_3, d_1). ^{31}P-{^{1}H} NMR spectrum (162 M, $CDCl_3$) δ_P ppm: 45.0 and 43.6 (two br. s, d_1–d_4).



7d

5-Decyloxy-2-ethoxy-3-(4-methoxyphenyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (7d). A mixture of four diastereoisomers d_1/d_2 and d_3/d_4 with the 3 : 2 ratio. Orange oil (78 %, 0.328 g). Found (%): C, 68.11; H, 8.14; P, 6.63. $C_{26}H_{37}O_5P$. Calculated (%): C, 67.81; H, 8.10; P, 6.73. IR spectrum (film) ν (cm^{-1}): 3255, 2929, 2247, 1729, 1610, 1513, 1469, 1253, 1197, 1096, 1038, 910, 799, 736. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ ppm, *J* Hz: 7.19 (br. dd, $^{3}J_{HH}$ 8.6, $^{4}J_{HH}$ 2.4, 2H, $H^{9,13}$, d_3/d_4), 7.11 (dd, $^{3}J_{HH}$ 8.6, $^{4}J_{HH}$ 2.5, 2H, $H^{9,13}$, d_1/d_2), 7.0 and 7.01 (two br. d, $^{3}J_{HH}$ 8.4 and 8.4, 1H, H^7, d_1–d_4), 6.91 and 6.89 (two br. d, $^{3}J_{HH}$ 8.6 and 8.8, 2H, $H^{10,12}$, d_1–d_4), 6.83 (m, $^{3}J_{HH}$ 8.4, $^{4}J_{HH}$ 2.4, 1H, H^6, d_1–d_4), 6.63 and 6.61 (two ddd, $^{4}J_{HH}$ 2.4, $^{4}J_{HH}$ 1.1, $^{4}J_{PH}$ 1.1 and $^{4}J_{HH}$ 2.4, $^{4}J_{HH}$ 1.1, $^{4}J_{PH}$ 1.1, 1H, H^4, d_1/d_2 and d_3/d_4), 4.58 (br. d, $^{2}J_{PH}$ 20.0, 1H, PCH, d_1), 4.35 (br. d, $^{2}J_{PH}$ 19.1, 1H, PCH, d_3/d_4), 4.29-4.37 (m, 2H, OCH_2, d_3/d_4), 3.99-4.07 (m, 2H, OCH_2, d_1/d_2), 3.85 (br. t, 2H, H^{14}, d_1–d_4), 3.82 and 3.80 (two s, 3H, OCH_3, d_1–d_4), 1.72 (br. m, 2H, H^{15}, d_1–d_4), 1.40 (t, 3H, $^{4}J_{PH}$ 7.1, CH_3, d_3/d_4), 1.22-1.35 (br. m, $H^{16\text{-}22}$, CH_2, d_1–d_4, CH_3, d_3/d_4), 1.03 (br. t, $^{3}J_{HH}$ 7.1, 3H, CH_3, d_1/d_2), 0.90 (br. t, $^{3}J_{HH}$ 6.9, H^{23}, d_1–d_4, CH_3, d_1/d_2). ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) δ_C ppm, *J* Hz: 159.33 and 159.26 (two d, $^{5}J_{PC}$ 3.5 and 3.1, C^{11}, d_1–d_4), 155.69 and 155.65 (d and s, $^{4}J_{PC}$ 1.8 and 0, C^5, d_1–d_4), 146.78 and 146.47 (two d, $^{2}J_{PC}$ 11.7 and 11.4, C^{7a}, d_1–d_4), 130.42 and 130.09 (two d, $^{3}J_{PC}$ 5.9 and 6.7, $C^{9,13}$, d_1–d_4), 129.65 and 128.30 (two d, $^{2}J_{PC}$ 7.4 and 7.0, C^{3a}, d_1–d_4), 126.47 and 125.57 (two d, $^{2}J_{PC}$ 6.6 and 9.4, C^8, d_1–d_4), 115.79 and 115.58 (two s, C^6, d_1–d_4), 114.60 and 114.35

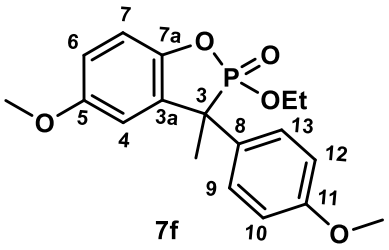
(two d, $^{4}J_{PC}$ 2.7 and 2.9, $C^{9,13}$, d_1–d_4), 114.03 and 113.91 (two d, $^{3}J_{PC}$ 10.7 and 12.0, C^{7}, d_1–d_4), 113.29 and 113.03 (two d, $^{3}J_{PC}$ 16.7 and 15.9, C^{4}, d_1–d_4), 68.80 and 68.76 (two s, C^{14}, d_1–d_4), 64.39 and 63.88 (two d, $^{2}J_{PC}$ 7.2 and 6.3, O**C**H$_2$, d_3, d_4), 63.73 and 63.27 (two d, $^{2}J_{PC}$ 7.5 and 7.0, O**C**H$_2$, d_1, d_2), 55.42 and 55.37 (two br. s, OCH$_3$, d_1–d_4), 43.83 and 43.09 (br. d and d, $^{1}J_{PC}$ 119.5 and 122.0, C^{3}, d_1–d_4), 32.02 (s, C^{15}, d_1–d_4), 29.83, 29.71, 29.69, 29.67 and 29.50 (five s, $C^{17–21}$, d_1–d_4), 29.16 (s, C^{16}, d_1–d_4), 22.80 (s, C^{22}, d_1–d_4), 16.63, 16.40, 16.30 and 16.13 (four d, $^{3}J_{PC}$ 5.5, 5.5, 5.6 and 5.6, CH$_3$, d_1–d_4), 16.24 (s, C^{23}, d_1–d_4). ^{31}P-{^{1}H} NMR spectrum (162 MHz, CDCl$_3$) δ_P ppm: 44.4 (br. s, d_3/d_4), 43.0 (br. s, d_1/d_2). HRMS (ESI) calcd for $C_{26}H_{38}O_5P$ $[M + H]^+$ 461.2451, found 461.2448.



7e

5-Decyloxy-2-ethoxy-3-(3,4,5-trimethoxyphenyl)-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (7e). A mixture of four diastereoisomers. The isomers d_1/d_2 and d_3/d_4 ratio was 1 : 1. Orange oil (80 %, 0.457 g). Found (%): C, 64.41; H, 8.07; P, 6.11. $C_{28}H_{41}O_7P$. Calculated (%): C, 64.60; H, 7.94; P, 5.95. IR spectrum, ν (cm^{-1}): 3306, 2927, 2855, 1727, 1591, 1463, 1331, 1232, 1191, 1127, 1031, 868, 811, 735, 647, 619. HRMS (ESI) calcd for $C_{28}H_{42}O_7P$ $[M + H]^+$ 521.2662, found 521.2659. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) δ ppm, *J* Hz: 7.0 and 7.01 (two dd, $^{3}J_{HH}$ 8.7, $^{4}J_{PH}$ 0.9 and $^{3}J_{HH}$ 8.7, $^{4}J_{PH}$ 0.9, 1H, H^{7}, d_1–d_4), 6.83 (m, $^{3}J_{HH}$ 8.7, $^{4}J_{HH}$ 2.7, 1H, H^{6}, d_1–d_4), 6.65 and 6.63 (two ddd, $^{4}J_{HH}$ 2.8, $^{4}J_{PH}$ 1.4, $^{4}J_{HH}$ 1.2 and $^{4}J_{HH}$ 2.8, $^{4}J_{PH}$ 1.3, $^{4}J_{HH}$ 1.3 1H, H^{4}, d_1/d_2 and d_3/d_4), 6.47 (d, $^{4}J_{HH}$ 2.7, 2H, $H^{9,13}$, d_1/d_2), 6.37 (d, $^{4}J_{HH}$ 2.4, 2H, $H^{9,13}$, d_3/d_4), 4.55 (br. d, $^{2}J_{PH}$ 21.3, 1H, PCH, d_1/d_2), 4.25-4.35 (m, 2H, OCH$_2$, d_3/d_4), 4.32 (br. d, $^{2}J_{PH}$ 19.3, 1H, PCH, d_3/d_4), 4.03-4.17 (m, 2H, OCH$_2$, d_1/d_2), 3.85 (br. t, 3H, H^{14}, d_1–d_4), 3.86, 3.82, 3.81 and 3.80 (four s, 9H, $C^{10–12}$–OCH$_3$, d_1–d_4), 1.77-1.66 (m, 2H, H^{15}, d_1–d_4), 1.40 and 1.34 (two t, $^{3}J_{HH}$ 7.1, CH$_3$, d_3/d_4), 1.22-1.32 (m, $H^{16–22}$, d_1–d_4), 1.04 and 0.87 (two br. t, $^{3}J_{HH}$ 7.1, CH$_3$, d_1/d_2), 0.88 (br. t, $^{3}J_{HH}$ 6.8, H^{23}, d_1–d_4). ^{13}C-{^{1}H} NMR spectrum (101 MHz, CDCl$_3$) δ_C ppm, *J* Hz: 155.55 and 155.58 (two br. s, C^{5}, d_1–d_4), 153.54 and 153.51 (br. d, $^{4}J_{PC}$ 3.6, $C^{10,12}$, d_1–d_4), 146.61 (d, $^{2}J_{PC}$ 11.6, C^{7a}, d_1/d_2), 146.20 (d, $^{2}J_{PC}$ 11.6, C^{7a}, d_3/d_4), 137.62 and 137.55 (two d, $^{5}J_{PC}$ 4.4 and $^{5}J_{PC}$ 3.9, C^{11}, d_1–d_4), 129.88 (d, $^{2}J_{PC}$ 6.3, C^{8}, d_1/d_2), 128.97 (d, $^{2}J_{PC}$ 9.4, C^{8}, d_3/d_4), 128.06 and 127.45 (two d, $^{2}J_{PC}$ 7.1 and $^{2}J_{PC}$ 6.4, C^{8}, d_1–d_4), 115.93 and 115.78 (two s, C^{6}, d_1–d_4), 113.98 and 113.94 (two d, $^{3}J_{PC}$ 10.6 and $^{3}J_{PC}$ 10.7, C^{7}, d_1–d_4), 113.17 and 112.97 (two d, $^{3}J_{PC}$ 16.5 and $^{3}J_{PC}$ 15.8, C^{4}, d_1–d_4), 106.17 and 106.15 (two d, $^{3}J_{PC}$ 6.0 and $^{3}J_{PC}$ 7.0, $C^{9,13}$, d_1–d_4), 68.73 and 68.68 (two s, C^{14}, d_1– d_4), 64.40 and 63.75 (two d, $^{2}J_{PC}$ 7.2 and $^{2}J_{PC}$ 7.2, OCH$_2$, d_1/d_2 and d_3/d_4), 60.90, 60.88, 60.73 and 60.71 (four s, C^{11}O**C**H$_3$, d_1–d_4), 56.24 and

56.10 (two s, $C^{10,12}$–O**C**H_3, d_1–d_4), 44.73 and 43.90 (two br. d, $^1J_{PC}$ 118.7 and $^1J_{PC}$ 121.9, C^3, d_1–d_4), 31.81 (s, C^{15}, d_1–d_4), 29.56, 29.54, 29.52, 29.35, 29.31 and 29.29 (six s, C^{20}, d_1+d_2), 29.29 (s, $C^{17–21}$, d_1–d_4), 29.23 (s, C^{15}, d_1+d_2), 25.98 (s, C^{21}, d_1–d_4), (s, C^{16}, d_1–d_4), 16.49 and 16.04 (two d, $^3J_{PC}$ 5.5 and $^3J_{PC}$ 6.0, CH_3, d_1–d_4), 14.10 (s, C^{23}, d_1–d_4). ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) δ_P ppm: 44.4 (br. s, d_3/d_4), 43.1 (br. s, d_1/d_2).



2-Ethoxy-5-methoxy-3-(4-methoxyphenyl)-3-methyl-3*H*-benzo[*d*][1,2]oxaphosphole 2-oxide (7f). A mixture of four diastereoisomers d_1/d_2 and d_3/d_4 with the ratio of 3 : 2 was obtained as yellow oil (76 %, 0.340 g). Found (%): C, 62.12; H, 6.33; P, 8.77. $C_{18}H_{21}O_5P$. Calculated (%): C, 62.07; H, 6.08; P, 8.89. IR spectrum, ν (cm^{-1}): 3235, 2935, 2837, 2057, 1713, 1608, 1514, 1455, 1253, 1197, 1102, 912, 799, 740, 648. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ ppm, *J* Hz: 7.01-7.14 (m, 2H, $H^{9,13}$, d_1–d_4), 7.08 (br. m, 1H, H^7, d_1–d_4), 6.90 (br. d, $^3J_{HH}$ 8.6, 1H, H^6, d_1–d_4), 6.77 (very br. m, 2H, $H^{10,12}$, d_1–d_4), 6.58 (br. s, 1H, H^4, d_1–d_4), 4.05-4.19 (m, 2H, OCH_2, d_1–d_4), 3.74 and 3.72 (two br. s, 6H, OCH_3, d_1–d_4), 1.76 (br. d, 3H, $^3J_{PH}$ 3.5, C^3CH_3, d_1–d_4), 1.40 (t, $^3J_{HH}$ 7.1, 3H, CH_3, d_3/d_4), 0.96 (br. t, $^3J_{HH}$ 7.1, 3H, CH_3, d_1/d_2). ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) δ_C ppm, *J* Hz: 158.15 (br. s, C^{11}, d_1/d_2), 155.54 (br. s, C^5, d_1/d_2), 146.19 (br. d, $^2J_{PC}$ 10.6, C^{7a}, d_1/d_2), 135.73 (br. m, C^{3a}, d_1/d_2), 132.50 (br. s, C^8, d_1/d_2), 129.08 and 128.64 (br. d and d, $^3J_{PC}$ 5.0 and 6.1, $C^{9,13}$, d_1/d_2), 113.83 (s, C^6, d_1/d_2), 113.82 and 113.79 (two d, $^3J_{PC}$ 11.2 and 10.9, C^7, d_1/d_2), 113.43 (br. s, $C^{10,12}$, d_1/d_2), 111.32 and 111.26 (two d, $^3J_{PC}$ 14.3 and 14.2, C^4, d_1/d_2), 62.51 (br. d, $^2J_{PC}$ 5.1, CH_2, d_1/d_2), 55.69 and 55.05 (two s, C^{11}–O**C**H_3 and C^5–O**C**H_3 d_1/d_2), 43.82 and 43.81 (two d, $^1J_{PC}$ 123.1 and 124.9, C^3, d_1/d_2), 23.50 (br. s, C^3–**C**H_3, d_1/d_2), 16.21 (d, $^3J_{PC}$ 6.3, CH_3, d_1/d_2). ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) δ_P ppm: 47.4 and 47.0 (two br. s, d_1/d_2, d_3/d_4).

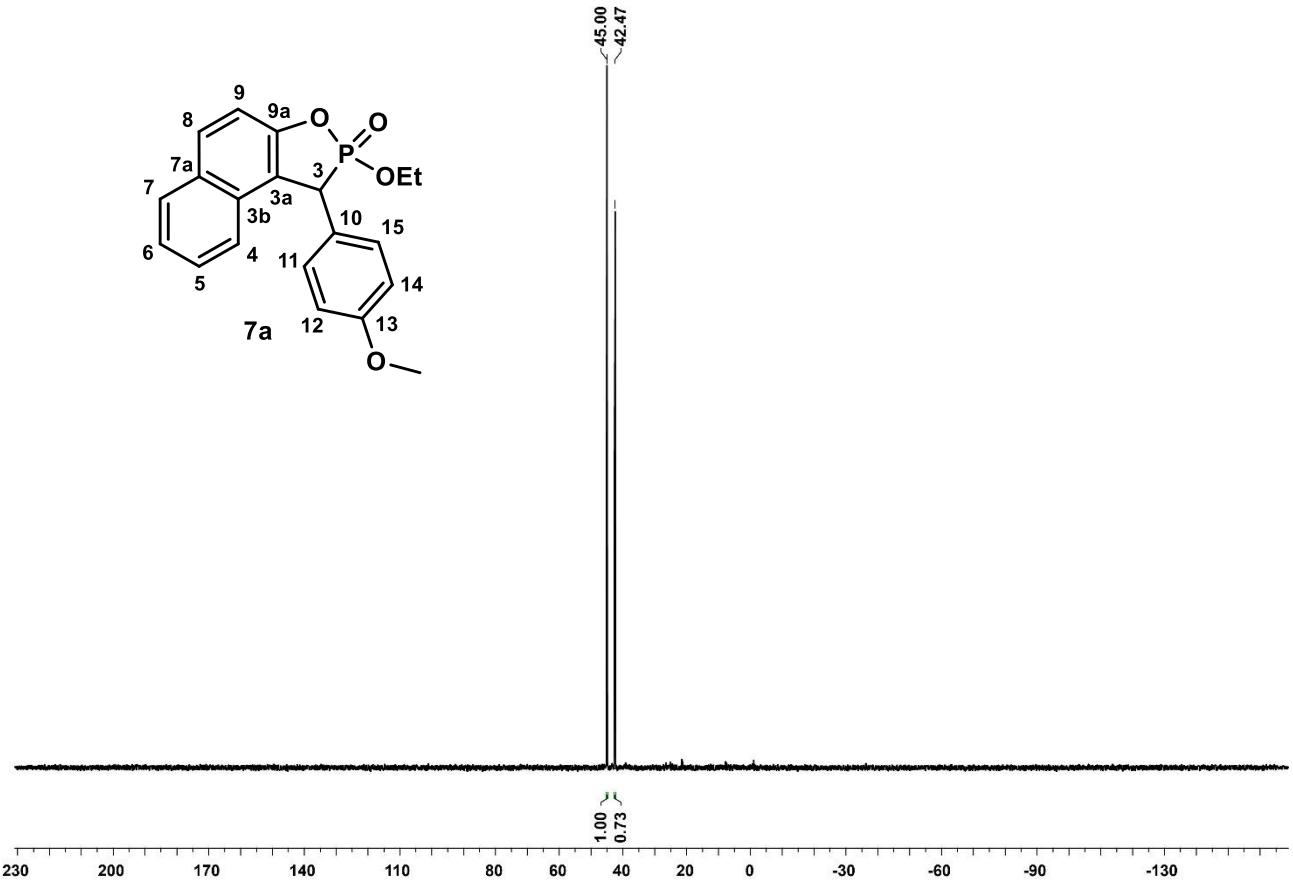


Figure S1. ^{31}P-{^{1}H} NMR spectrum (243 MHz, $CDCl_3$) of compound **7a**

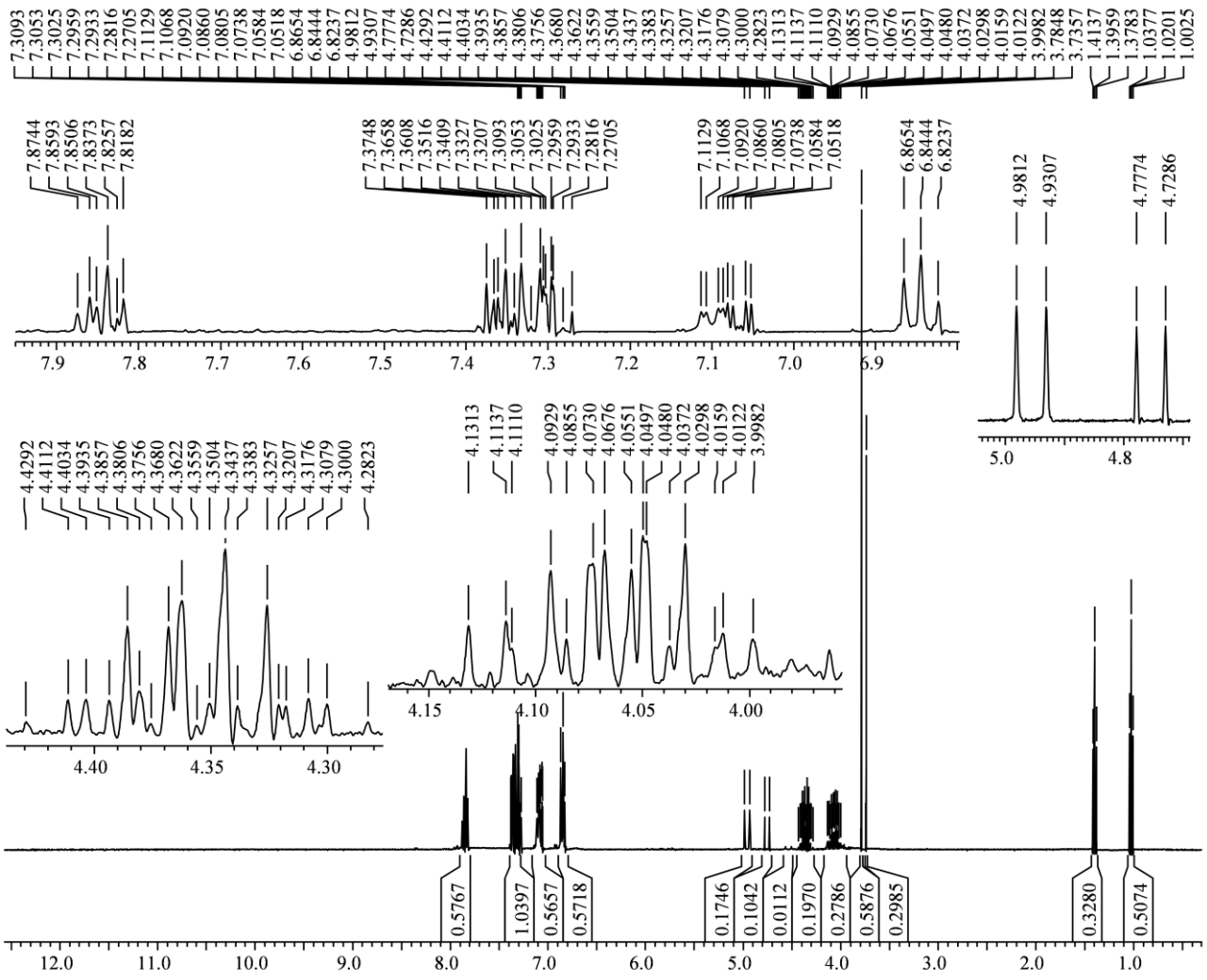
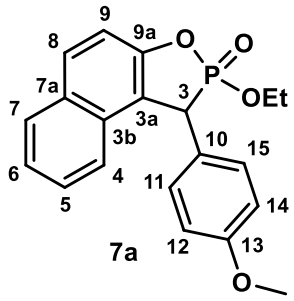


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7a**



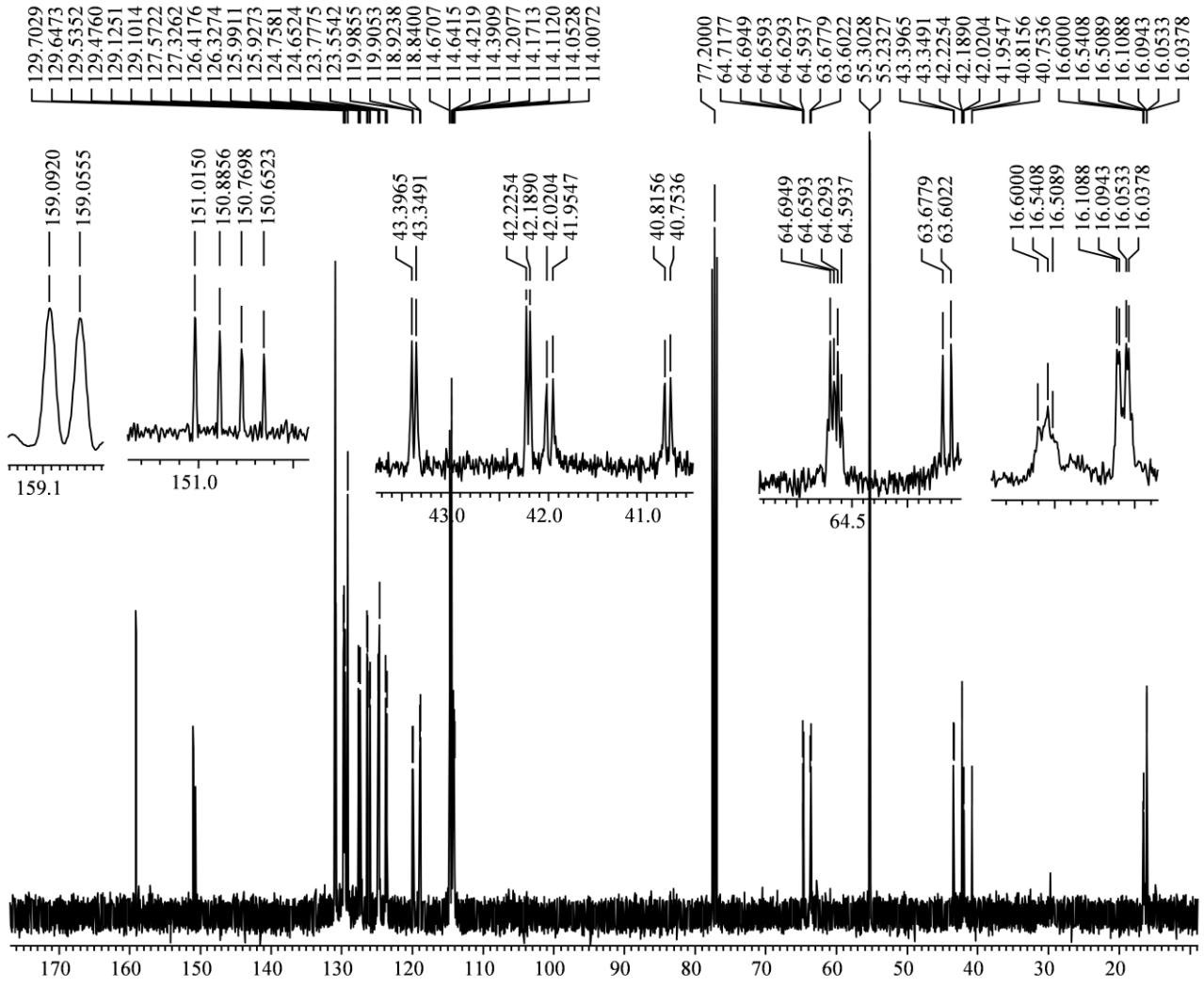
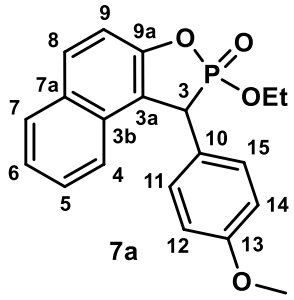


Figure S3. ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **7a**



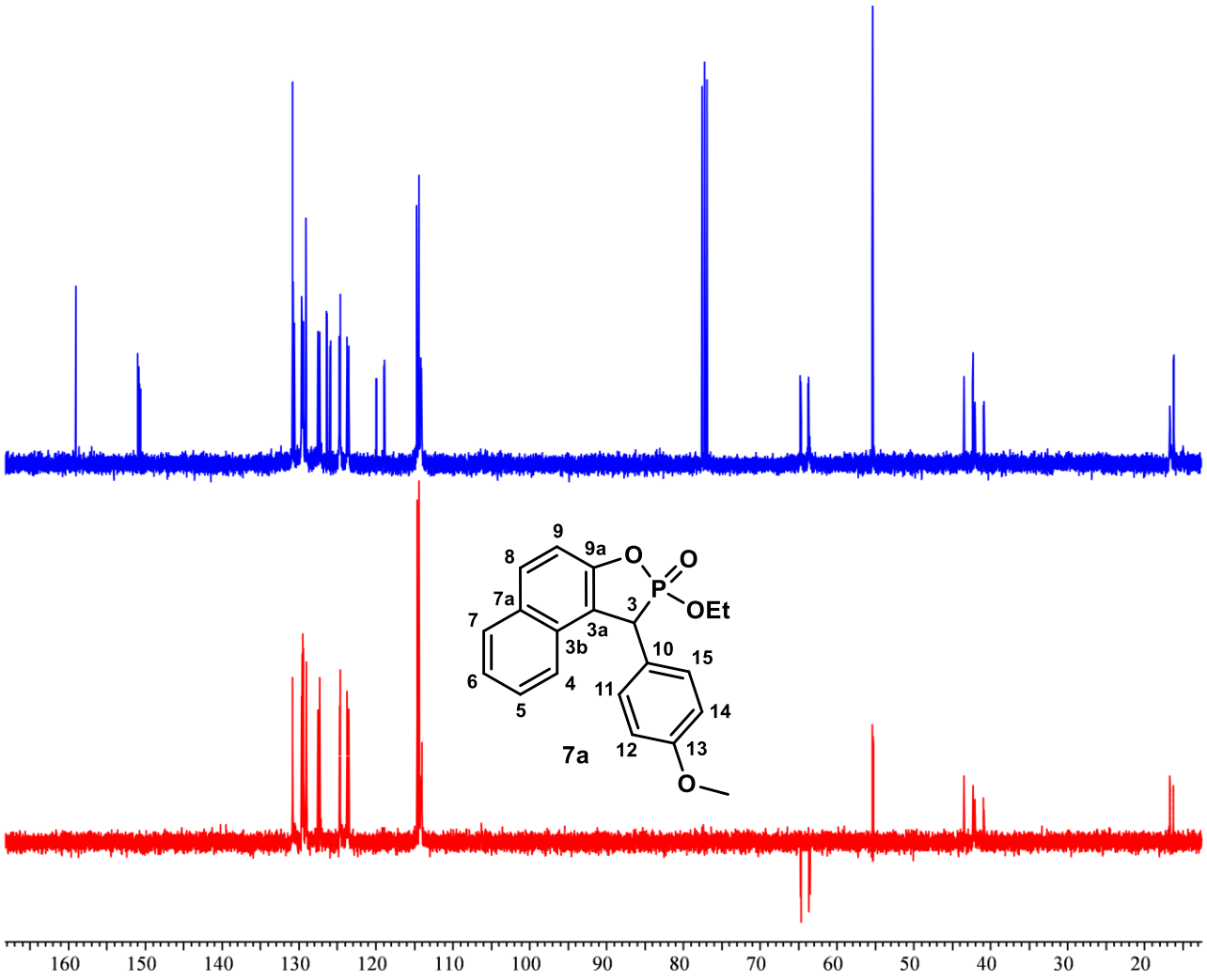


Figure S4. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (101 MHz, $CDCl_3$) of compound **7a**

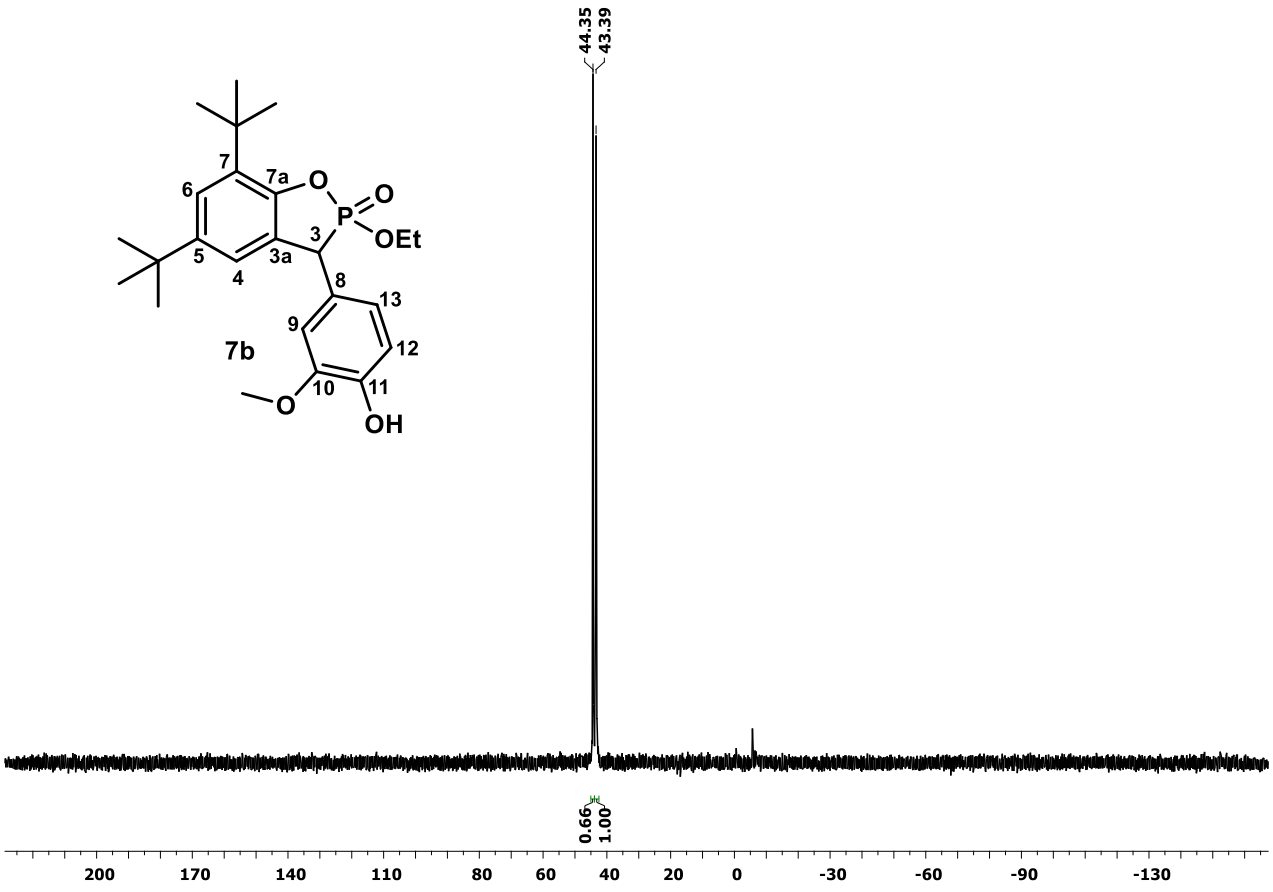


Figure S5. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **7b**

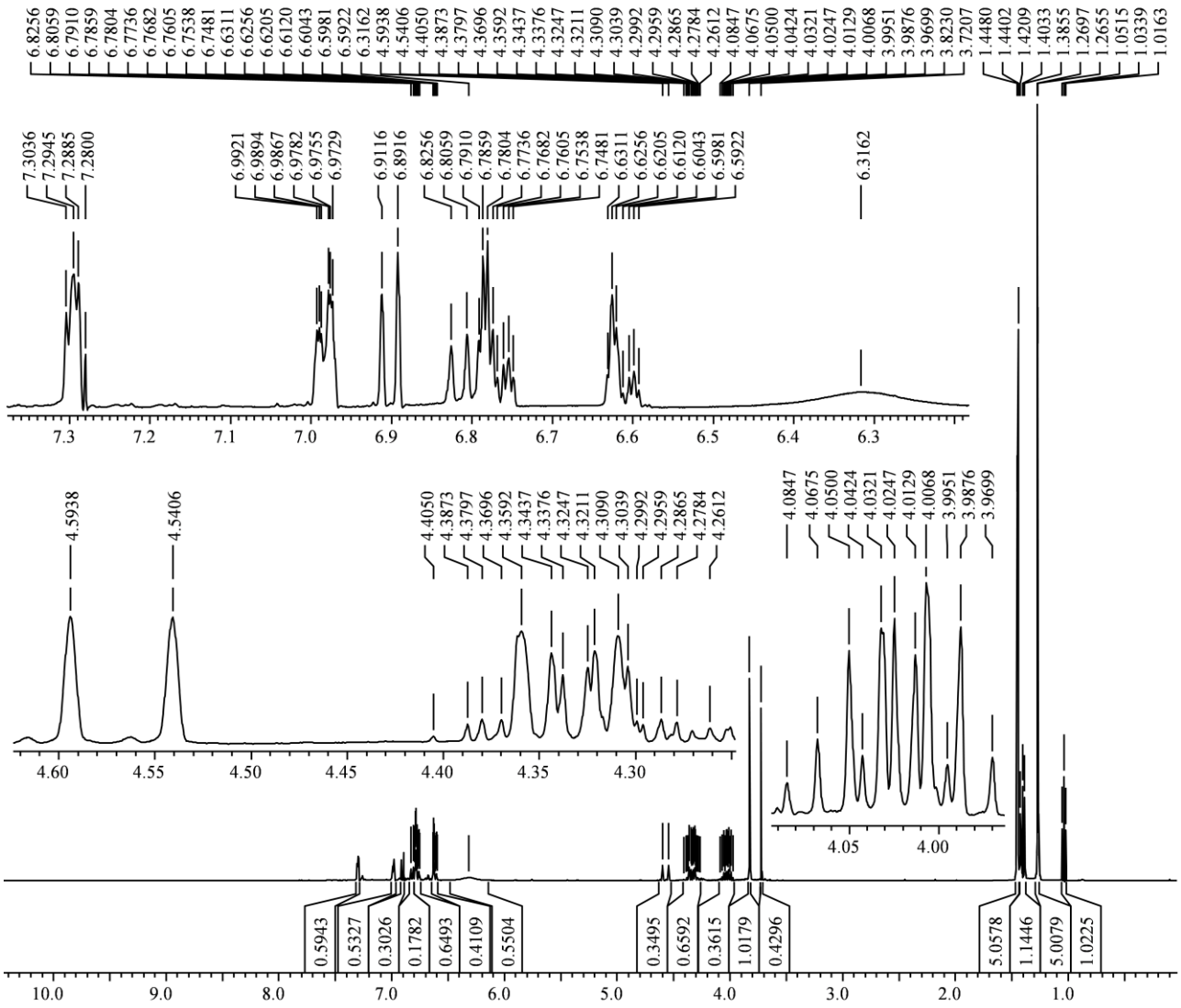
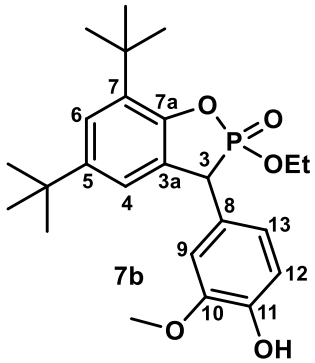


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7b**



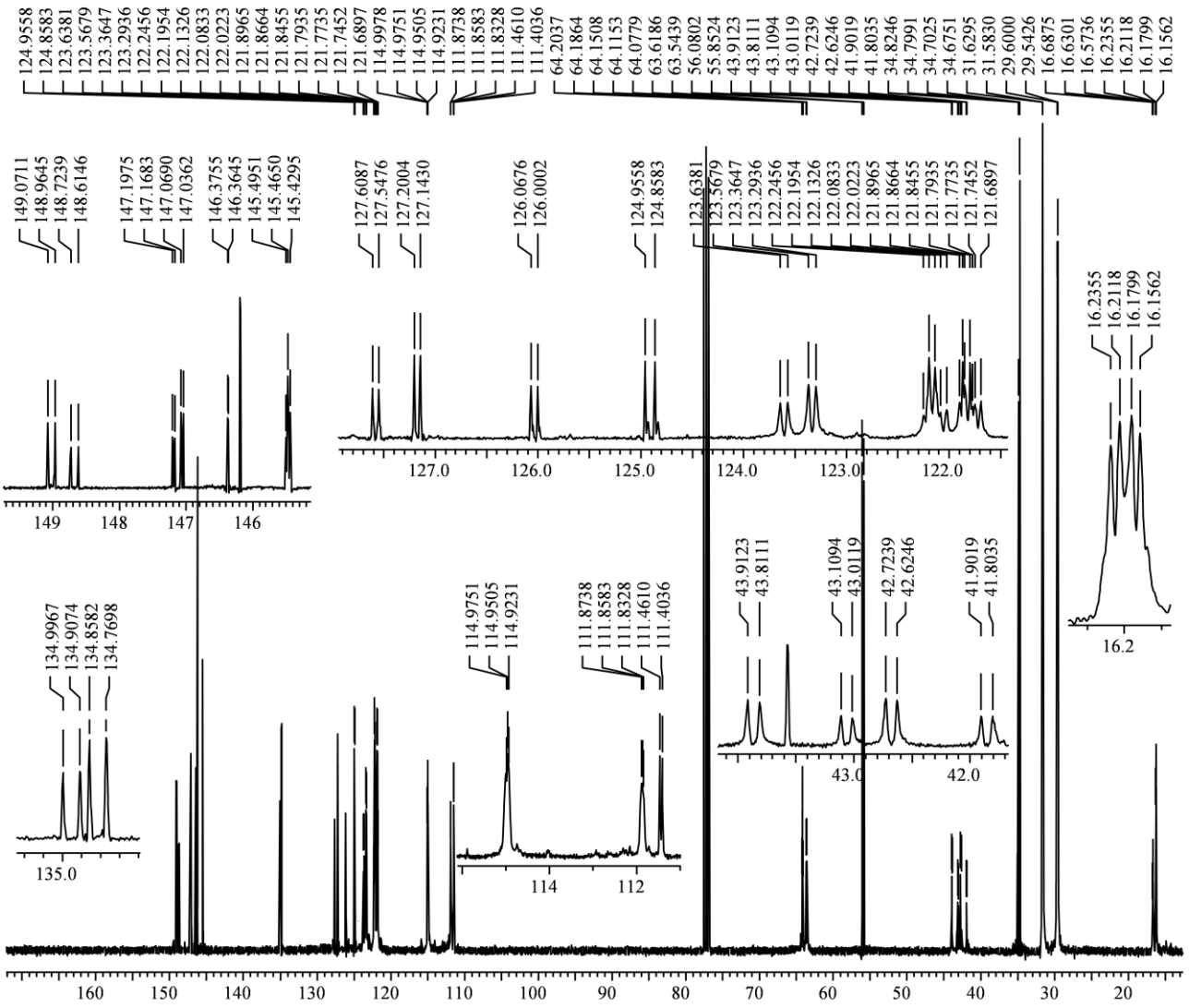
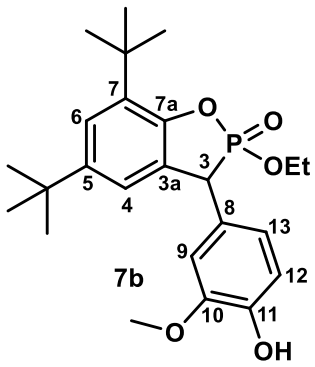


Figure S7. ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **7b**



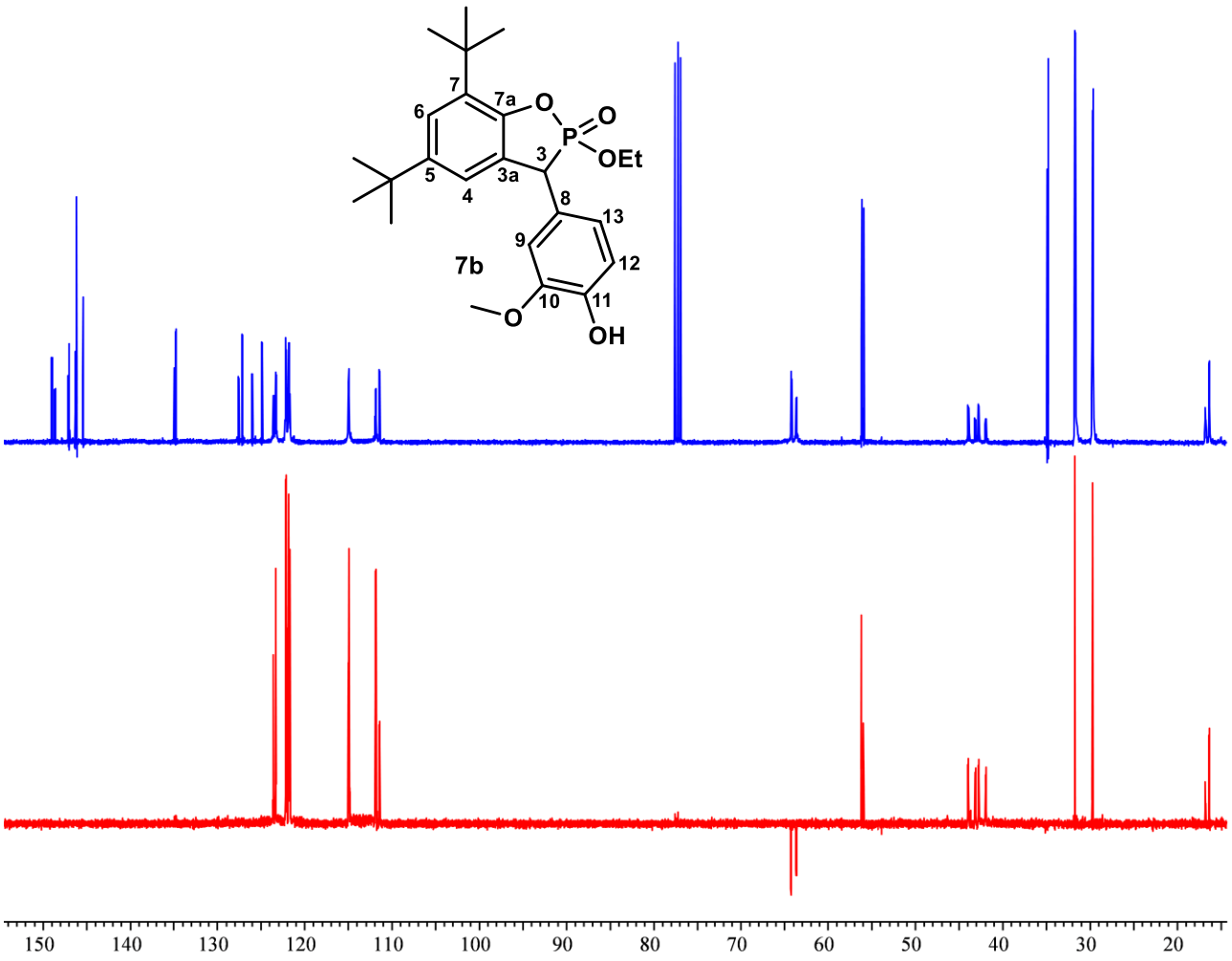


Figure S8. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (101 MHz, $CDCl_3$) of compound **7b**

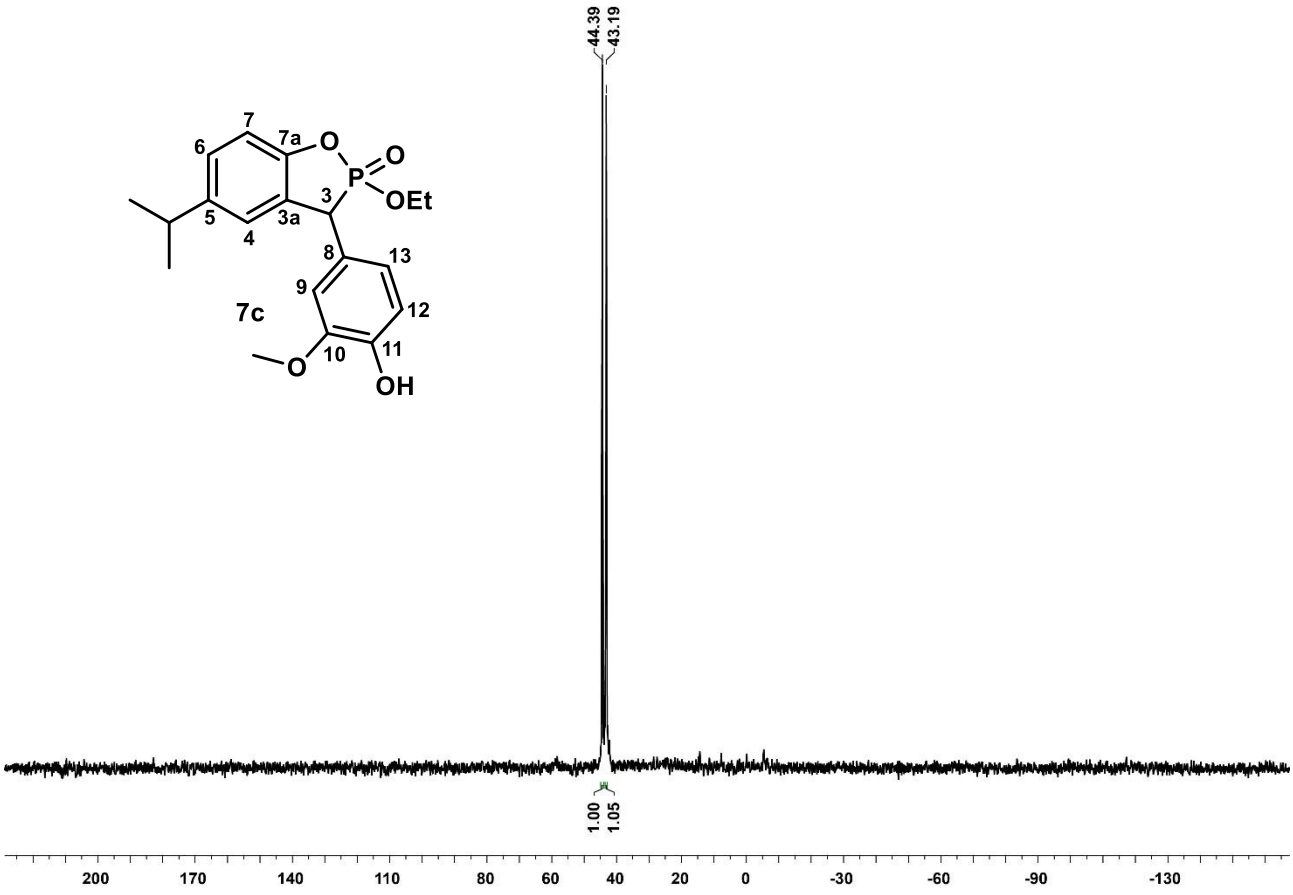


Figure S9. ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$) of compound **7c**

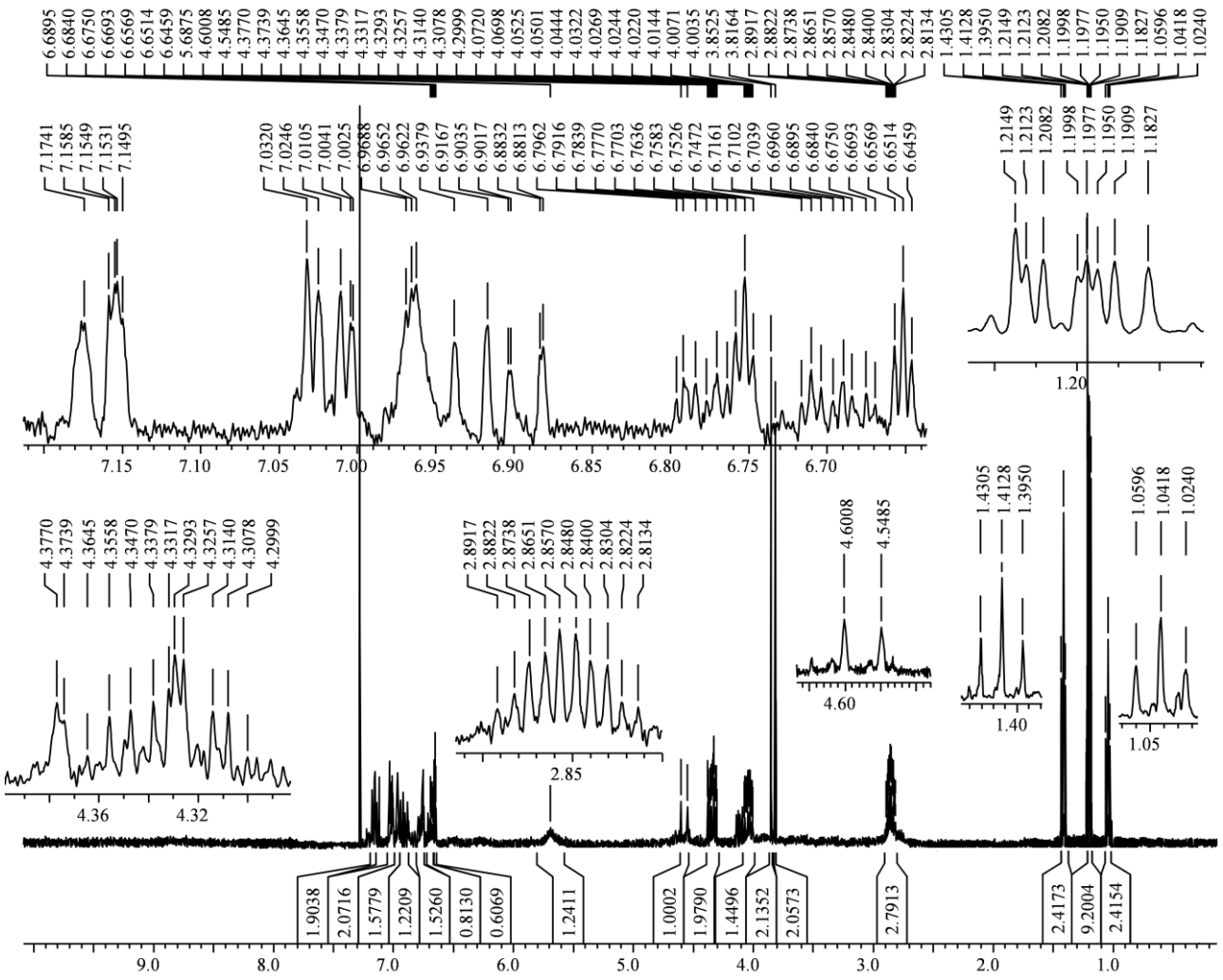
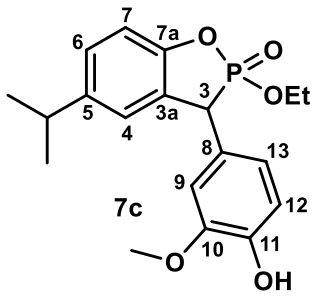


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7c**



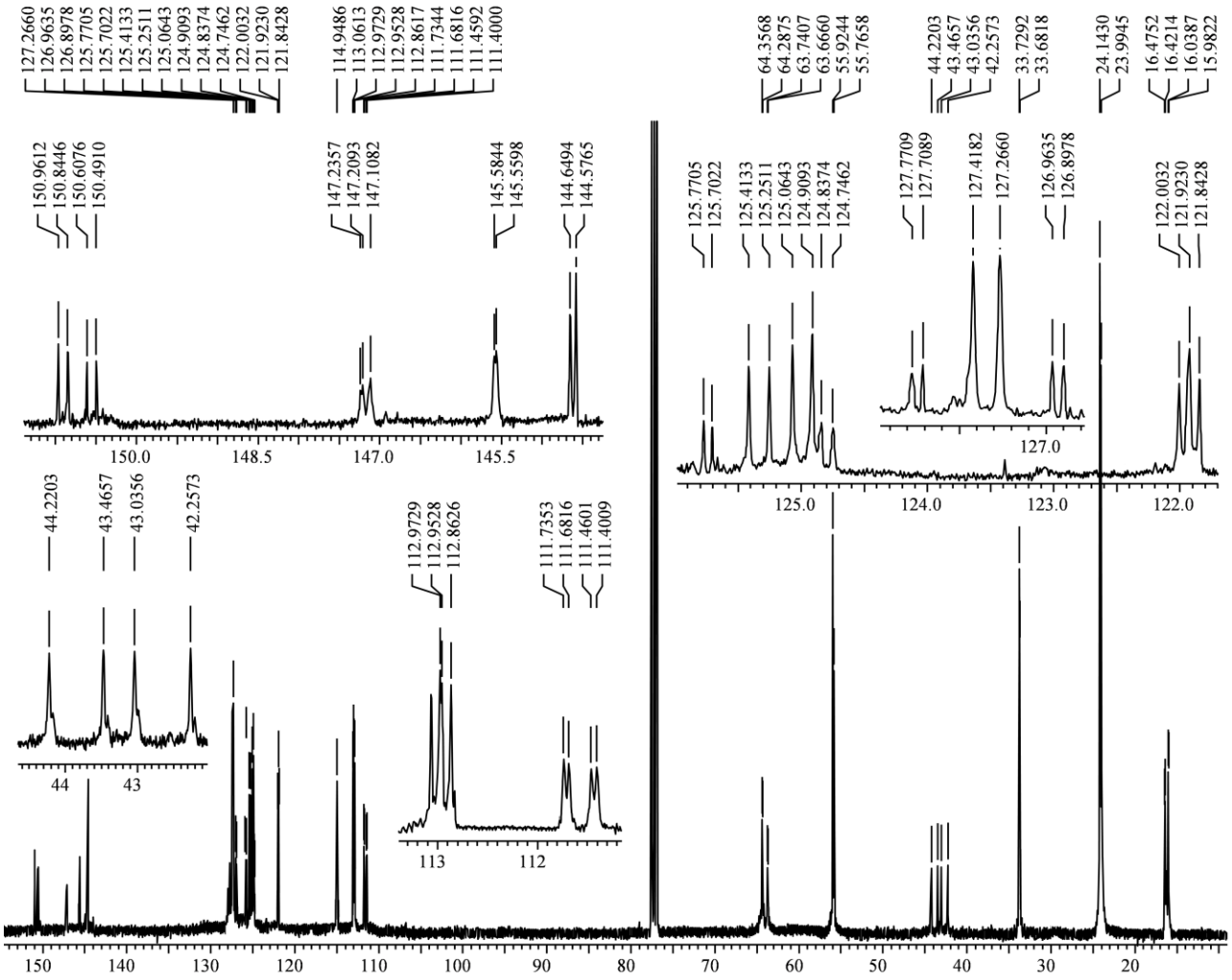
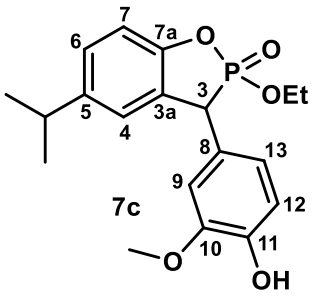


Figure S11. ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **7c**



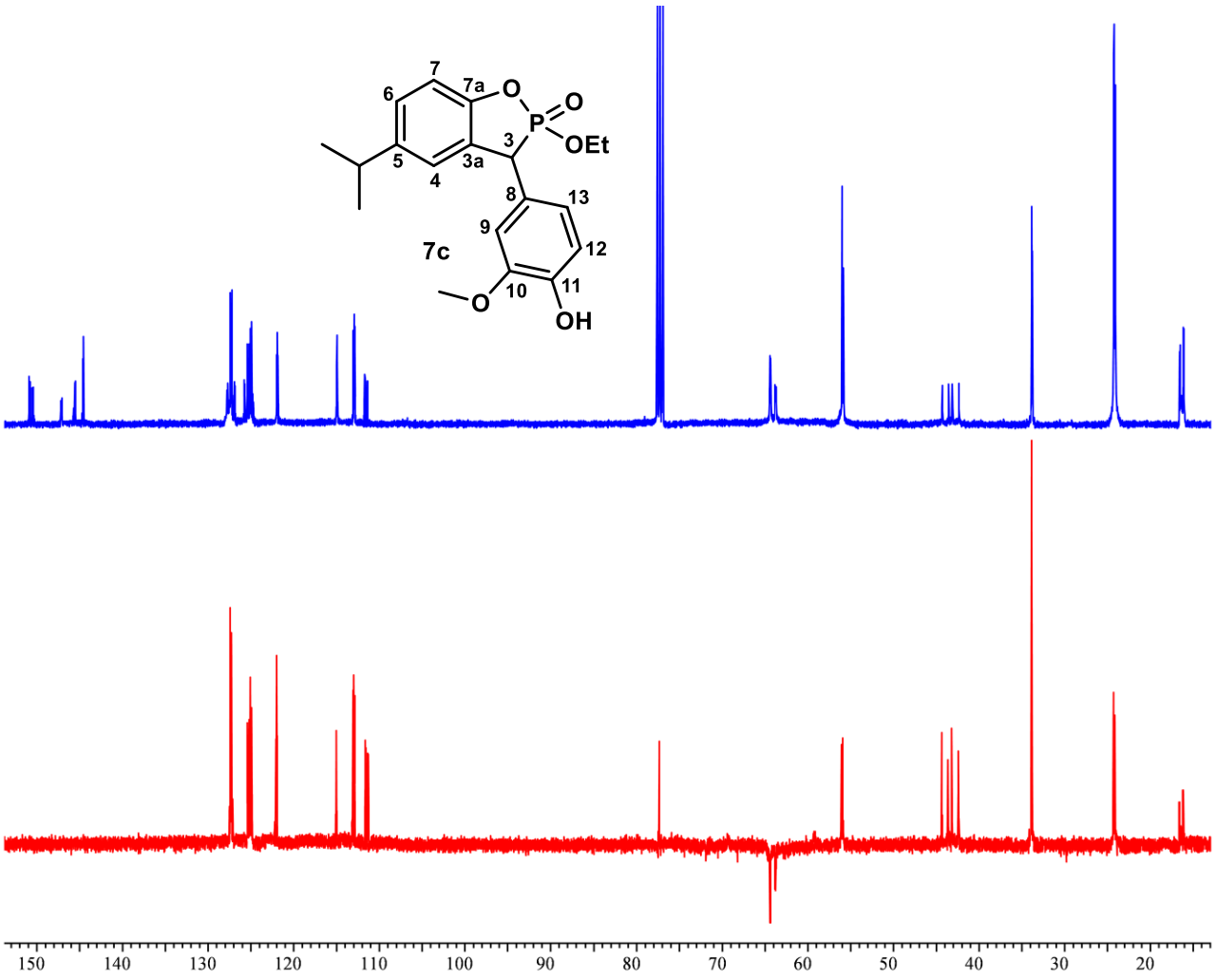


Figure S12. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (101 MHz, $CDCl_3$) of compound **7c**

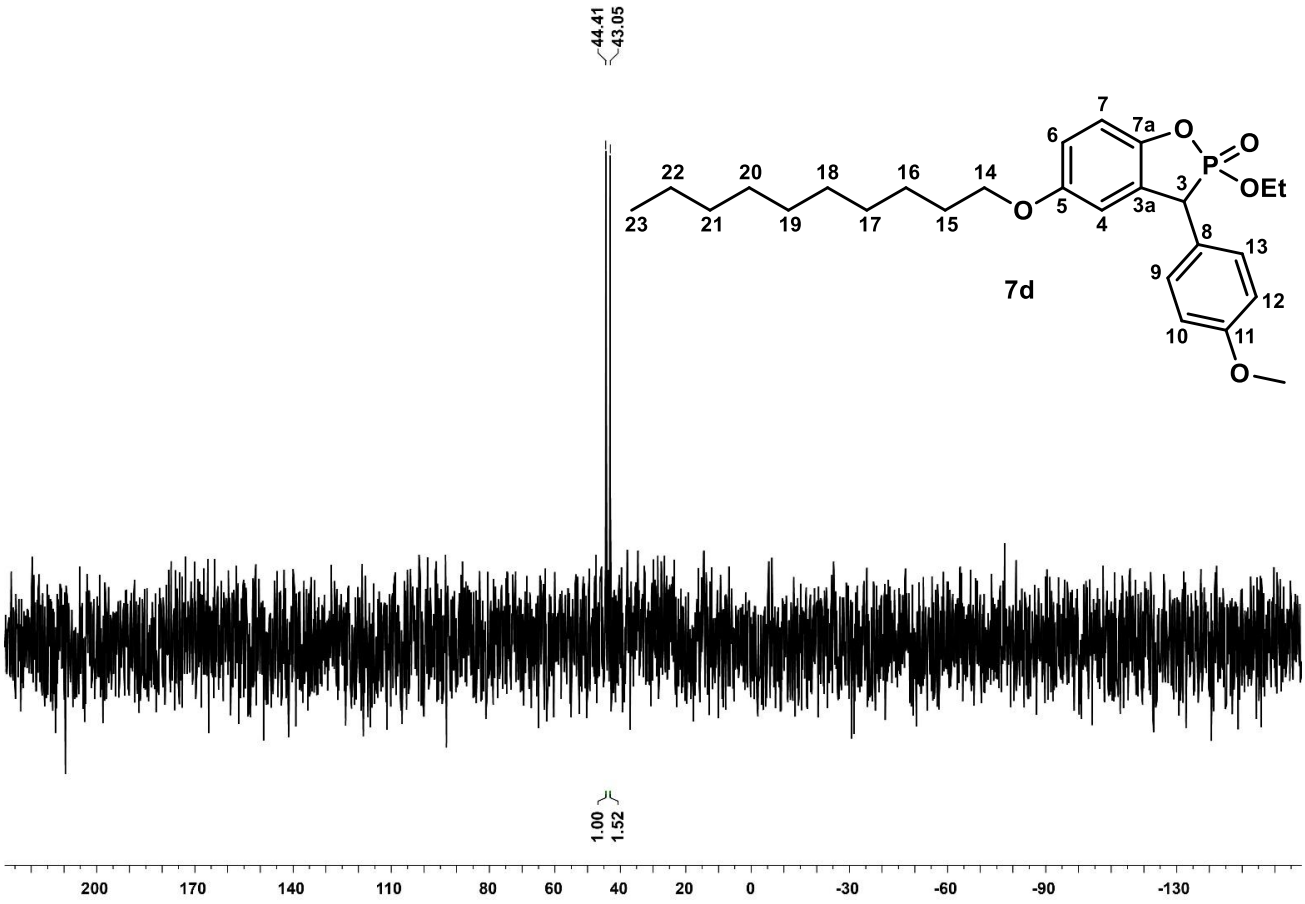


Figure S13. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **7d**

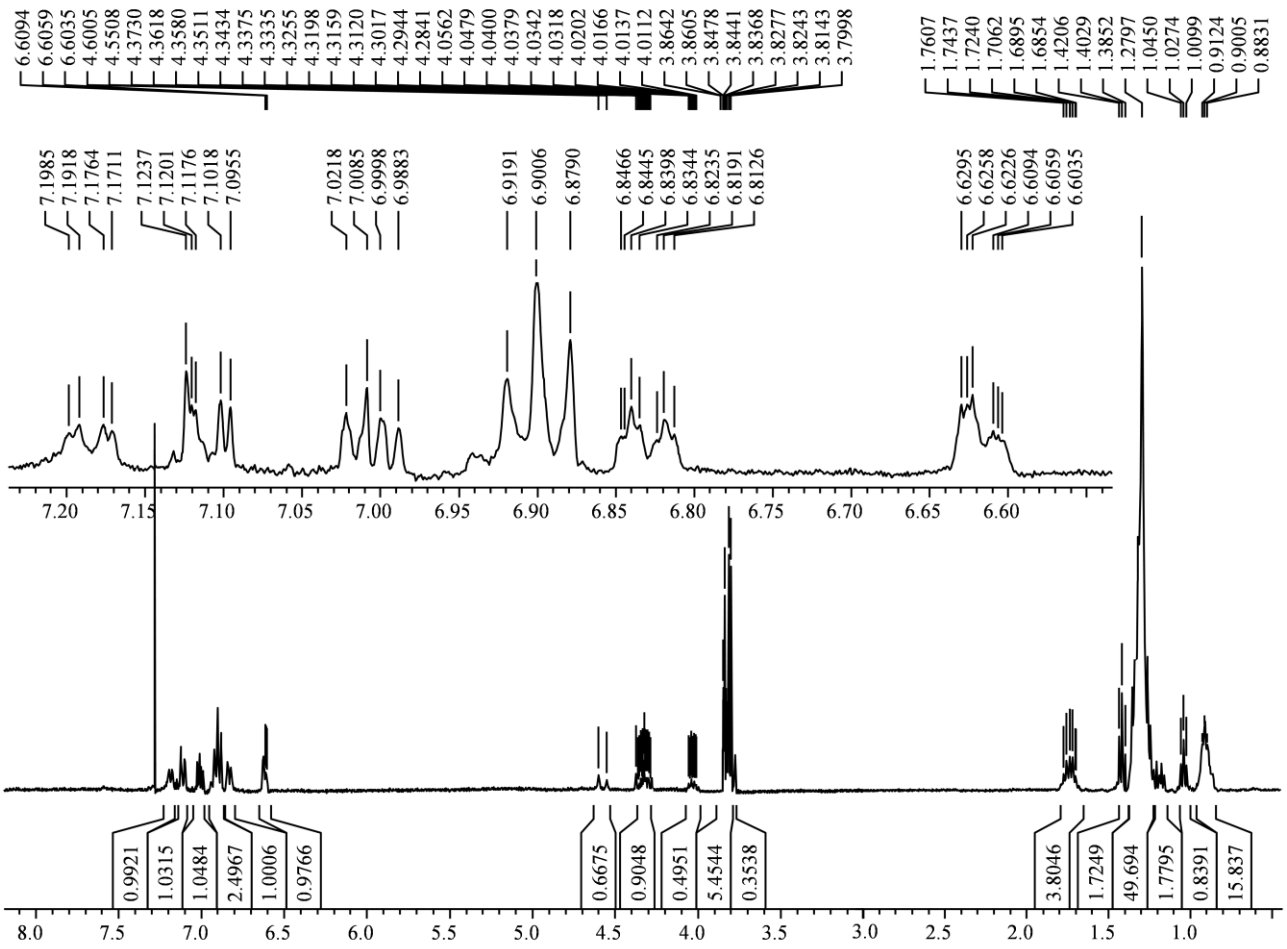
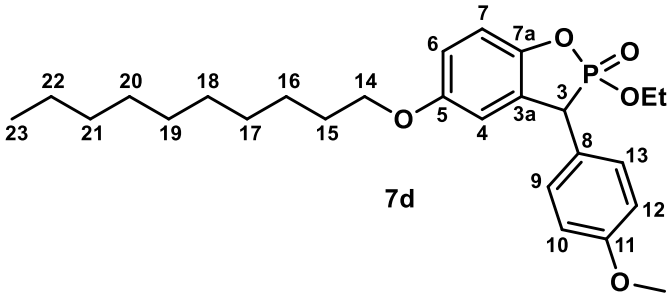


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7d**



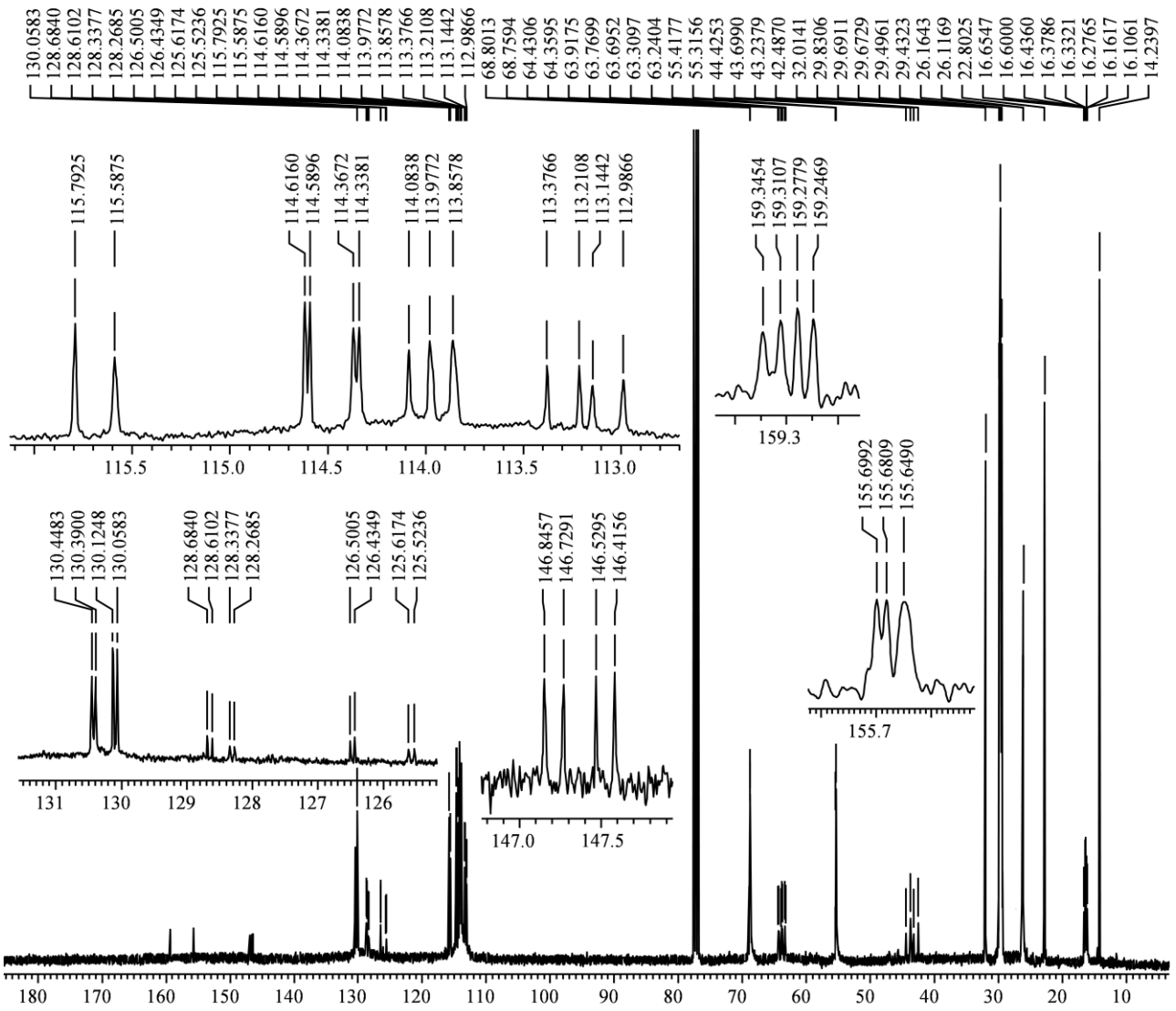
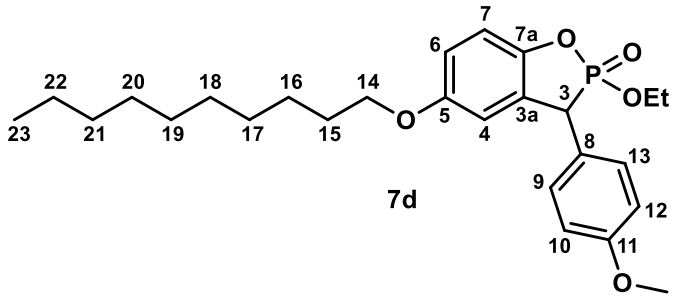


Figure S15. ^{13}C-{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **7d**



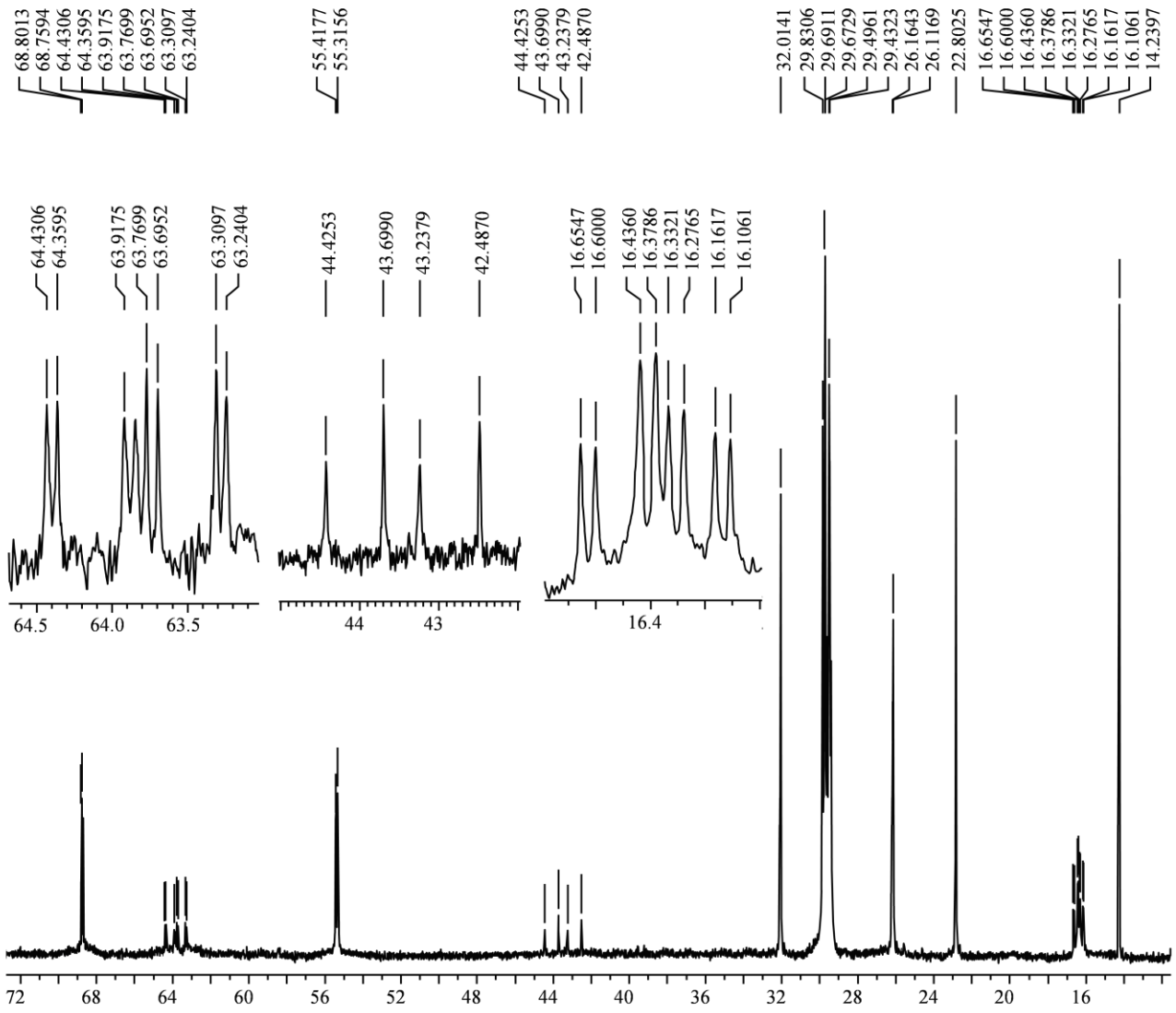
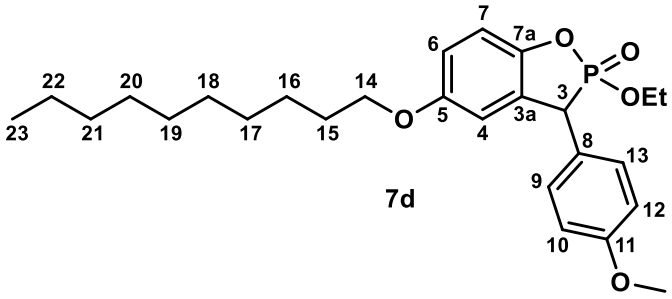


Figure S16. High-field part of ^{13}C-{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **7d**



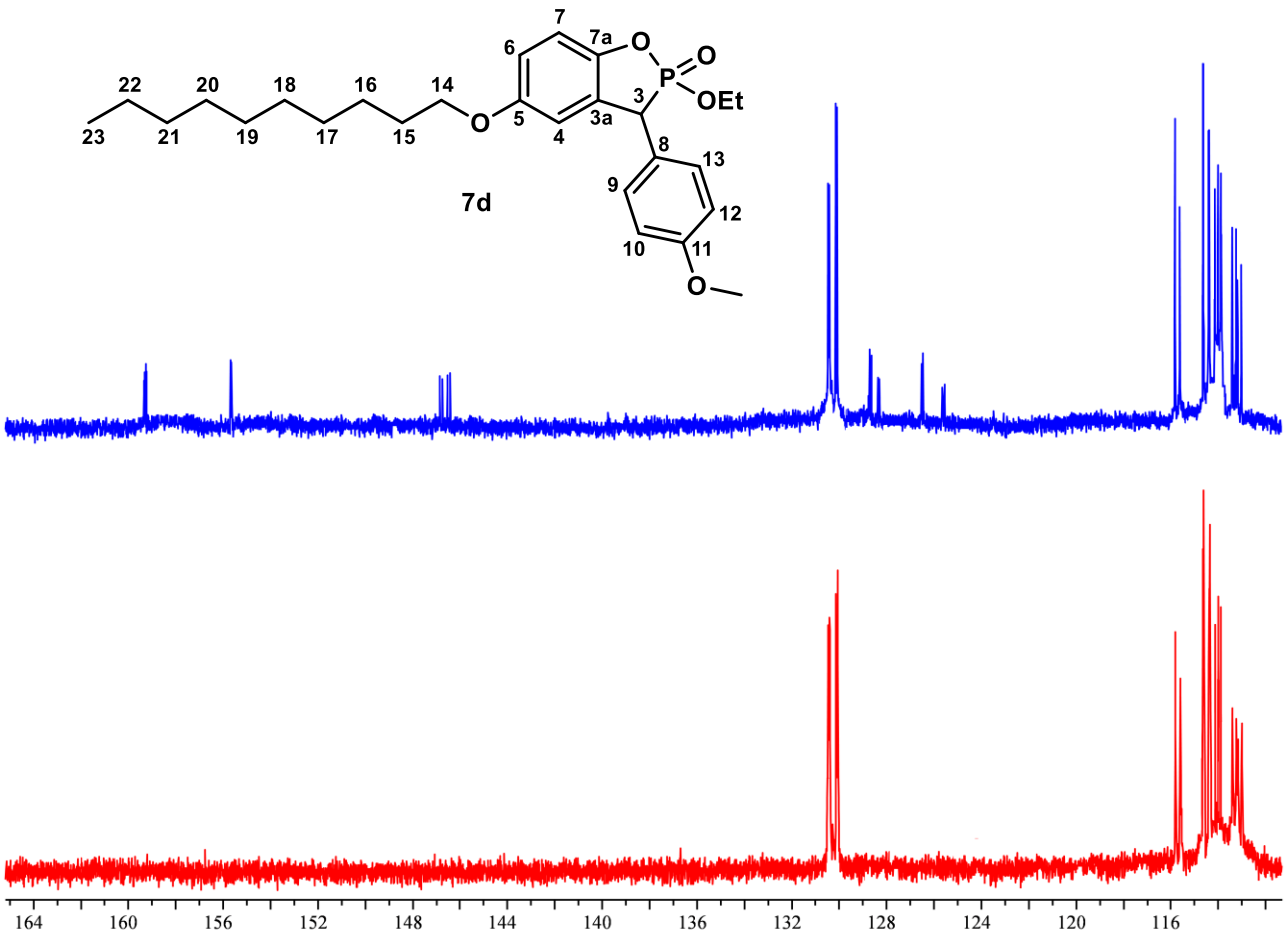


Figure S17. Low-field part of ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (100 MHz, $CDCl_3$) of compound **7d**

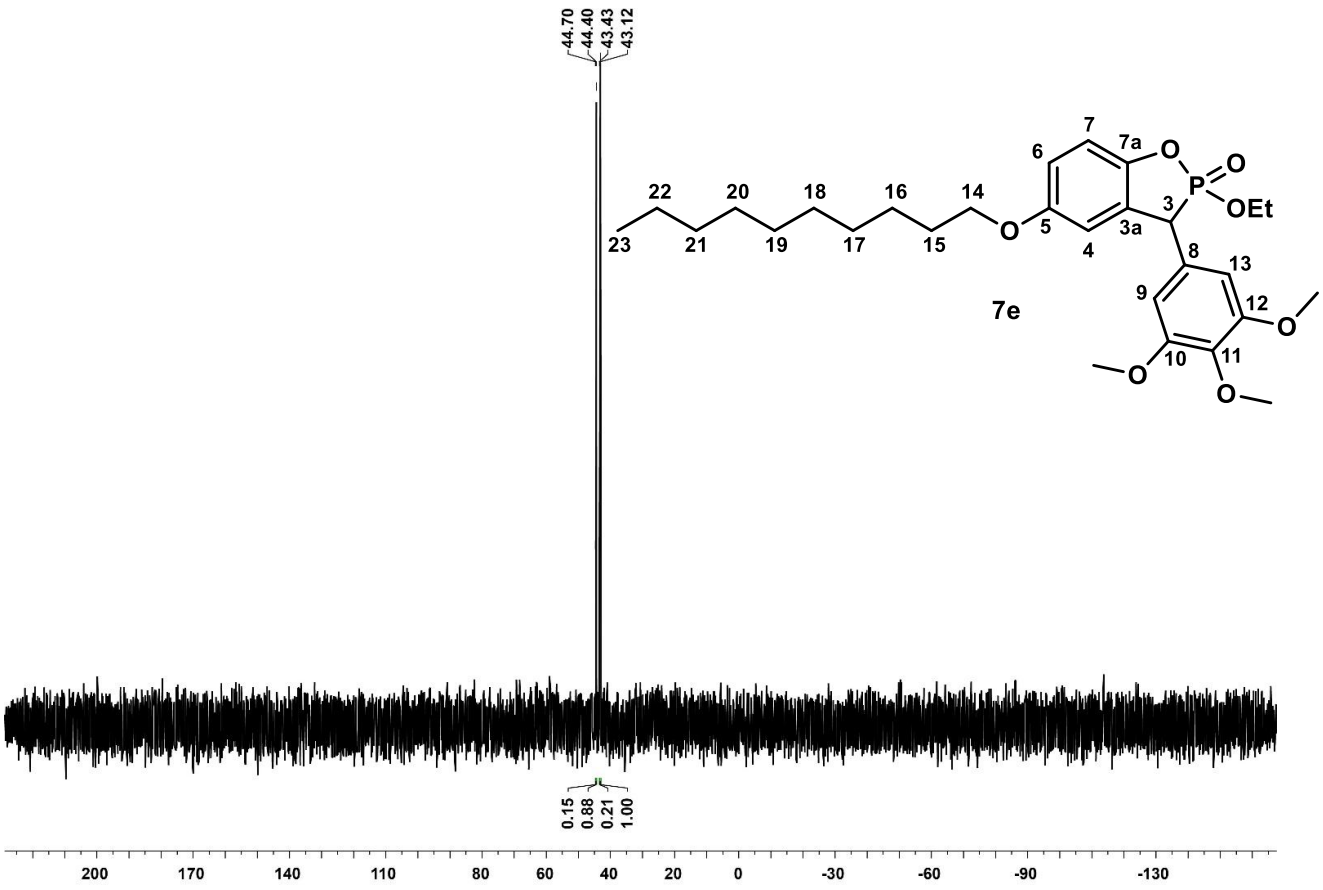


Figure S18. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **7e**

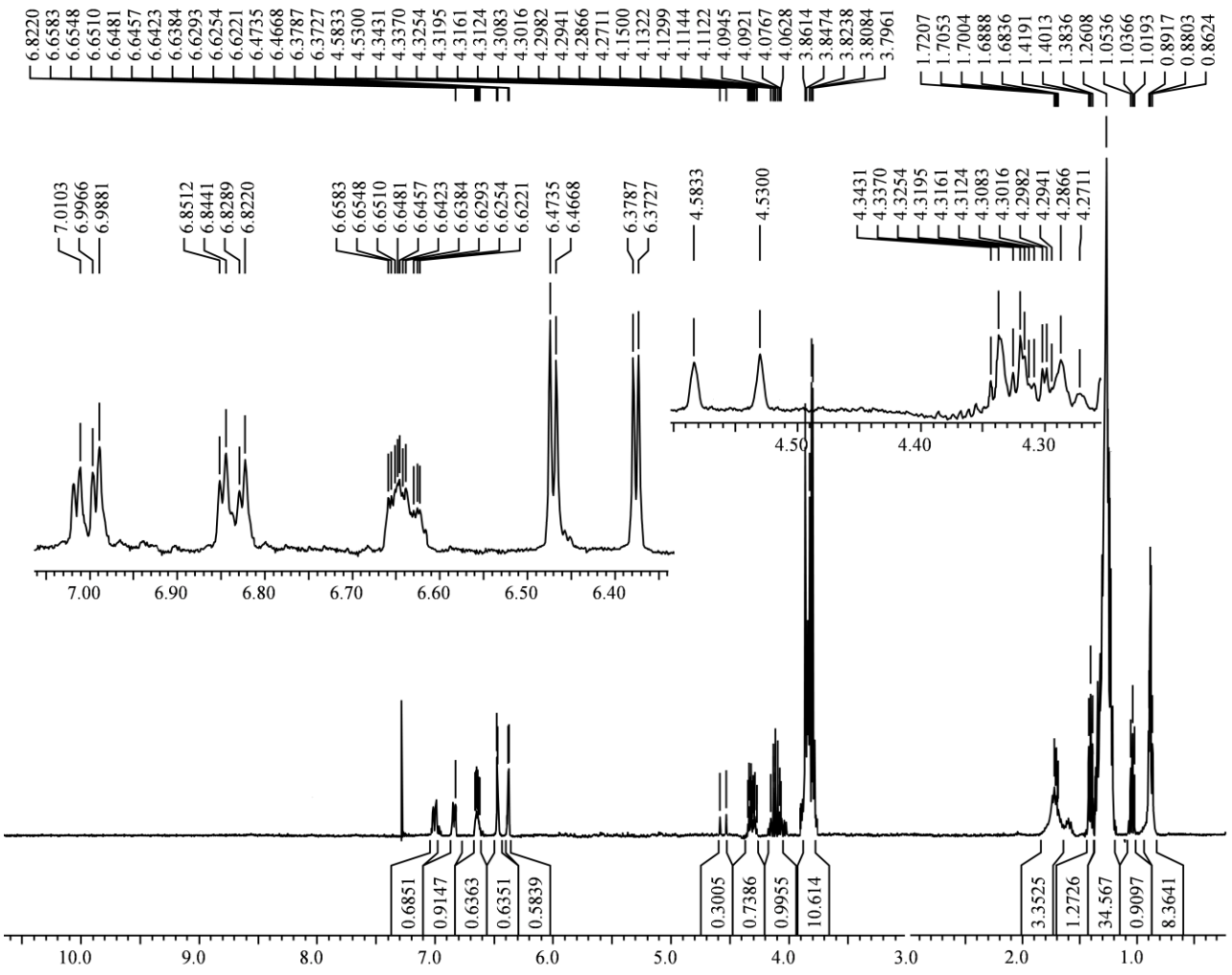
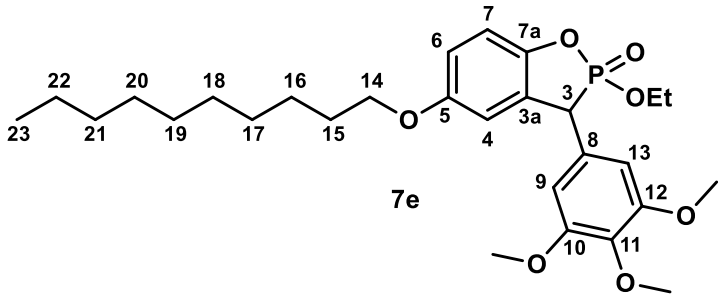


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7e**



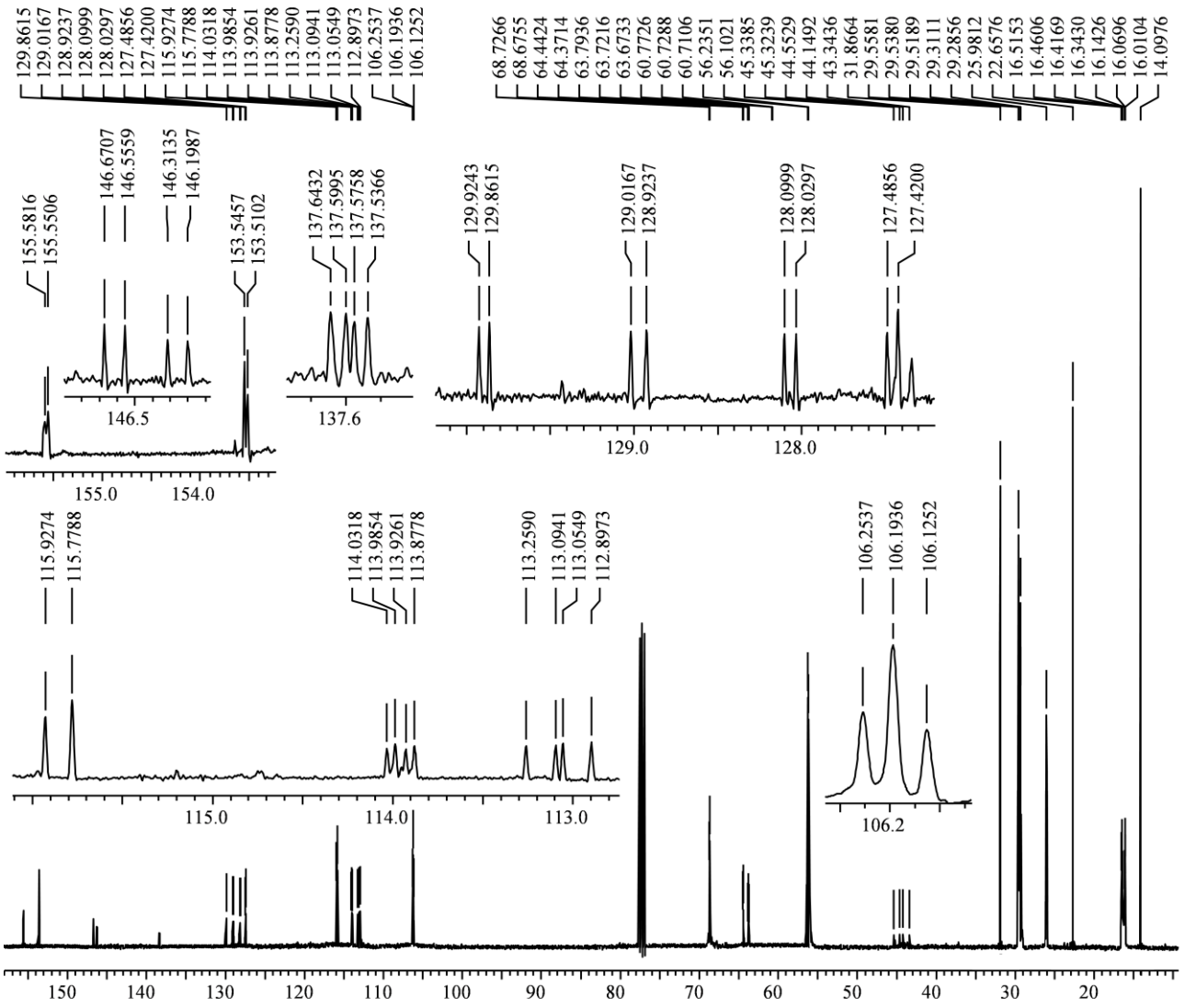
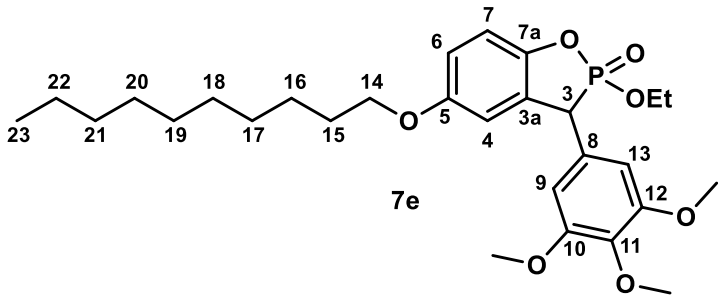


Figure S20. ^{13}C-{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **7e**



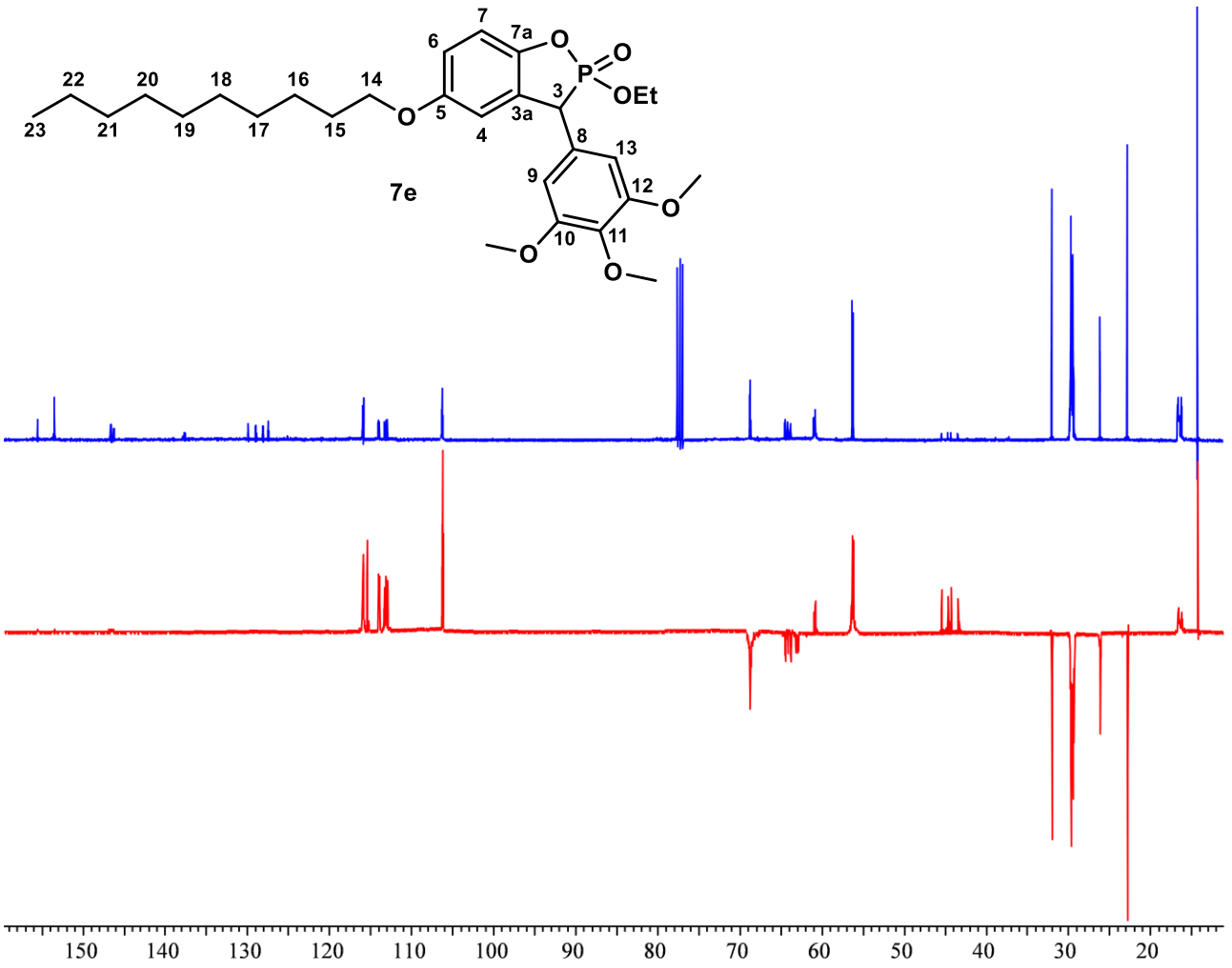


Figure S21. ^{13}C-{^{1}H} and ^{13}C-{^{1}H}-dept NMR spectra (100 MHz, $CDCl_3$) of compound **7e**

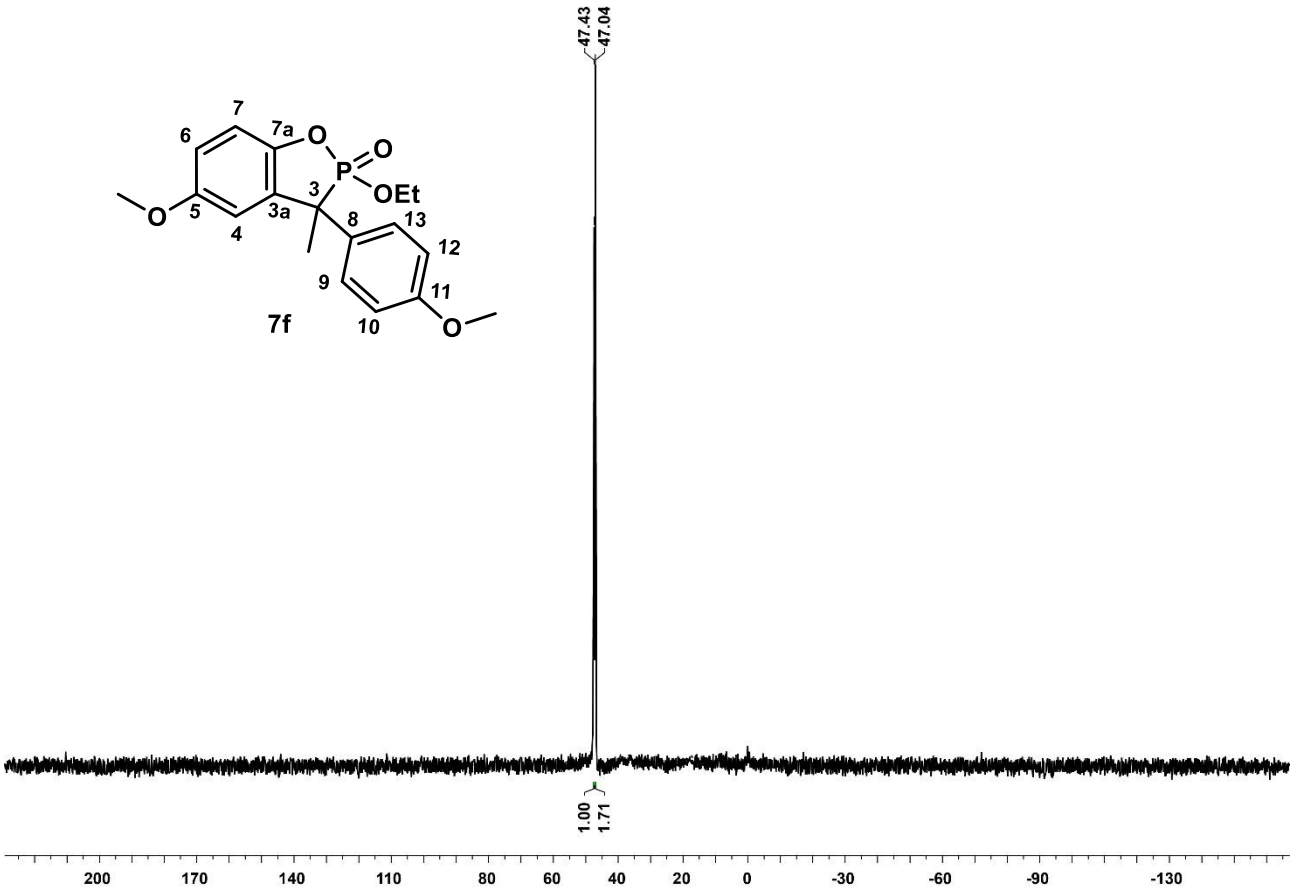


Figure S22. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **7f**

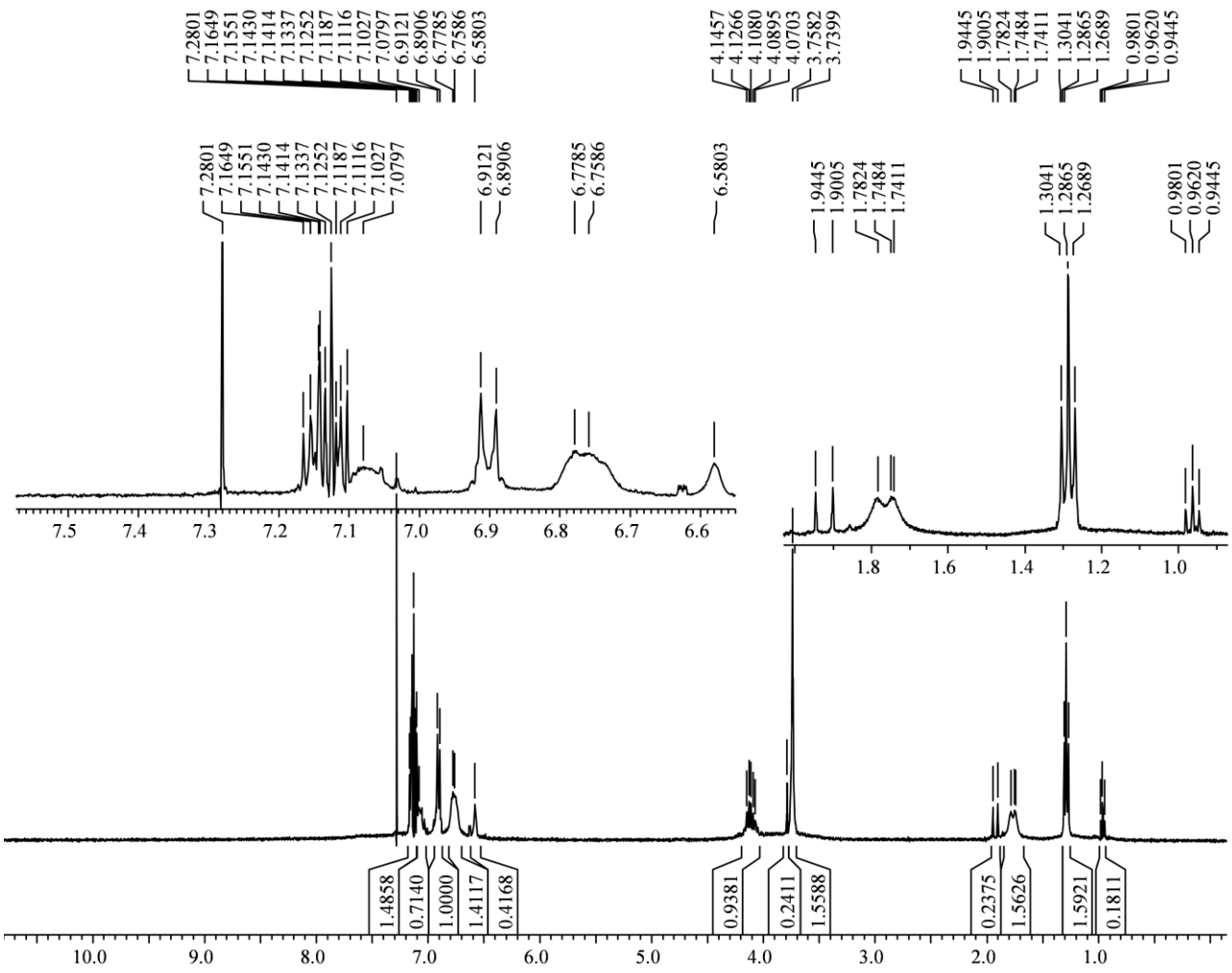
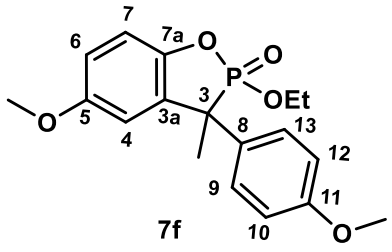


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7f**



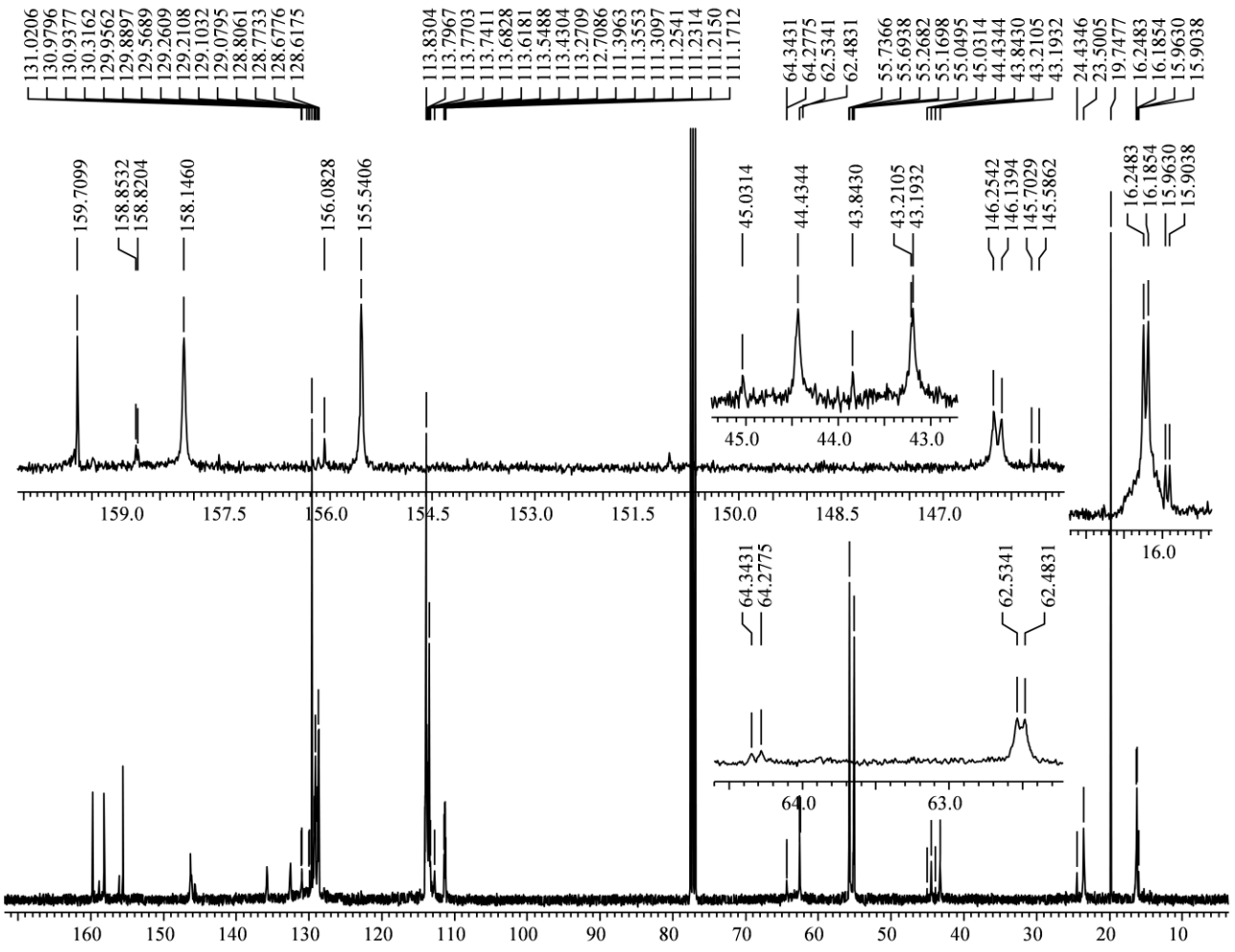
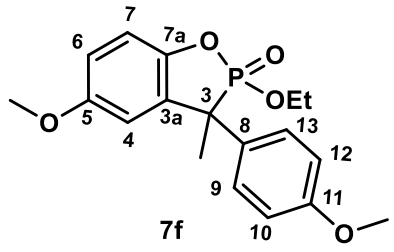


Figure S24. ^{13}C-{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **7f**



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