Electronic Supplementary Information

Base promoted synthesis of activated cyclopropanes bearing homologated carbonyl groups via tandem Michael addition-intramolecular enolate trapping

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General Information

THF was freshly distilled before use from $LiAlH_4$, dichloromethane was distilled from CaH_2. $CHCl_3$, dichloroethane and AcOEt were dried over molecular sieves (Aldrich Molecular Sieves, 3 Å, 1.6 mm pellets, activated under vacuum at 200°C overnight). Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel plates (0.25 mm) and visualised by UV light and *p*-anisaldehyde in EtOH/10% H_2SO_4. Flash chromatography was performed on Merck silica gel (60, particle size: 0.040–0.063 mm). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker DRX 400 spectrometer at room temperature in $CDCl_3$ as solvent. Chemical shifts for protons are reported using residual $CHCl_3$ as internal reference (δ=7.26 ppm). Carbon spectra were referenced to the shift of the ^{13}C signal of residual $CHCl_3$ (δ=77.0 ppm). Phosphorus spectra were calibrated on 85% H_3PO_4. Optical rotation of compound **3b** was performed on a Jasco Dip-1000 digital polarimeter using the Na lamp (582 nm). FT-IR spectra were recorded as thin films on KBr plates using Bruker Vertex 70 spectrometer and absorption maxima are reported in wavenumber (cm^{-1}). Elementary analyses were performed using a CHNS elementary analyzer. Melting points were measured on a digital Electrothermal 9100 apparatus.

Petrol ether (PE) refers to light petroleum ether (boiling point 40-60°C). Anhydrous toluene and all reactants (with exception of enones **1** and cinchona derived thioureas[1]) were purchased from Aldrich and used as received. Commercial *m*-CPBA (77% grade) was dissolved in CH_2Cl_2 and dried over Na_2SO_4, then crystallized with PE/Et_2O mixture at -20°C.

Enantiomeric excess of cyclopropane **3b** was determined by HPLC (Waters-Breeze 2487, UV dual λ absorbance detector and 1525 Binary HPLC Pump) using Daicel Chiralcel OD-H column.

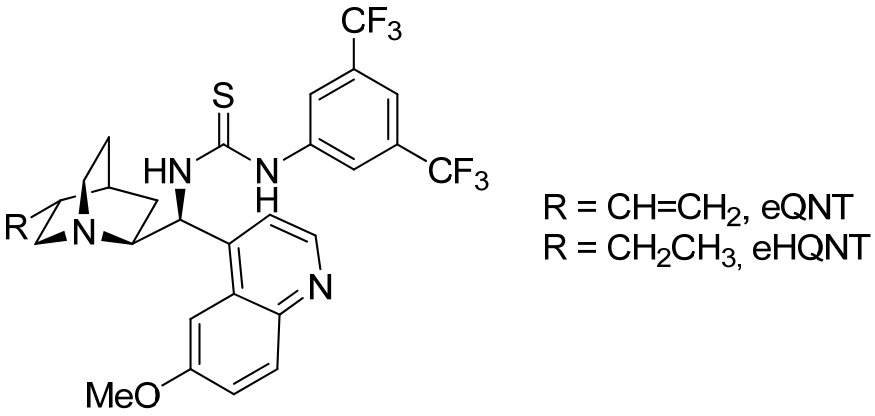
[1] a) For synthesis of cinchona derived thioureas see: B. Vakulya, S. Varga, A. Csámpai, T. Soós *Org. Lett.* **2005**, *7*, 1967-1969.

Experimental procedures and compounds characterization

General procedure for synthesis of cyclopropanes 3

Diphenylphosphinate **1** (0.10 mmol), 1,3-indandione (16 mg, 0.11 mmol) and K_2CO_3 (14 mg, 0.10 mmol) were mixed in dry $CHCl_3$ (2.0 mL). The violet coloured reaction mixture was stirred at room temperature for the appropriate time, then it was directly purified by flash chromatography (eluent PE/ ethyl acetate 9:1) to give products **3b-h**. Traces of 1,3-indandione in the product were removed by a second flash chromatography. Same procedure was adopted for the synthesis of cyclopropane **3a** using Meldrum's acid as nucleofile and piperidinemethanol as promoting base.

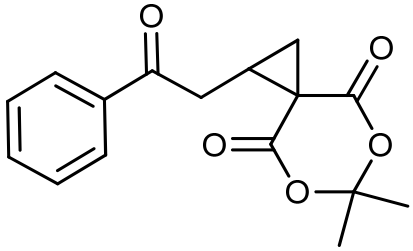
Structures of cinchona-based thioureas



Procedure for the asymmetric cyclopropanation of compound 1a

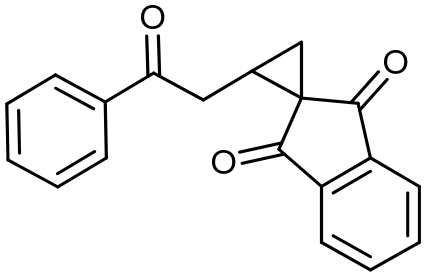
A sample vial charged with a mixture of (*E*)-4-oxo-4-phenylbut-2-en-1-yl diphenylphosphinate **1a** (36 mg, 0.10 mmol), 1,3-indandione (16 mg, 0.11 mmol) and appropriate cinchona alkaloid (0.10 mmol) in anhydrous toluene (2.0 mL) was stirred at room temperature for 1.5 h. The violet reaction mixture was directly purified by flash chromatography (eluent PE/ ethyl acetate 9:1) to give cyclopropane **3b**.

6,6-Dimethyl-1-(2-oxo-2-phenylethyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (3a)



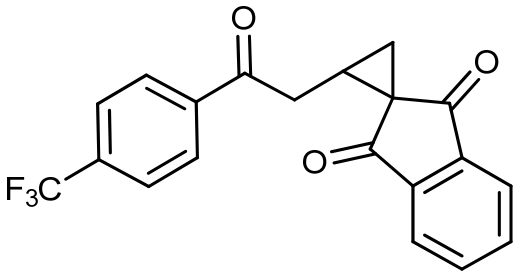
White wax. FTIR ν_{max} cm^{-1} 2924, 2853, 1738, 1687, 1597, 1449, 1394, 1337, 1206, 969, 757, 690, 660. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, 2H, J= 7.3 Hz), 7.58 (t, 1H, J= 7.84 Hz), 7.47 (t, 2H, J= 7.8 Hz), 3.63-3.50 (m, 2H), 2.84-2.76 (m, 1H), 2.31 (dd, 1H, J_1= 3.8 Hz, J_2= 9.3 Hz), 1.96 (dd, 1H, J_1= 3.8 Hz, J_2= 9.0 Hz), 1.90 (s, 3H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.3, 168.1, 166.6, 136.1, 133.6, 128.7, 128.0, 105.5, 36.1, 33.8, 28.2, 27.8, 27.7, 27.5. Elemental analysis calculated for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.83; H, 5.80.

2-(2-Oxo-2-phenylethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3b)



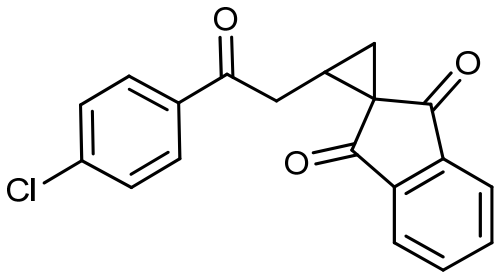
White solid, m.p. 74.0-75.2°C. $[\alpha]_D^{26}$ = +76.1 (*c* 0.8, $CHCl_3$), *ee* 67%. FTIR ν_{max} cm^{-1} 1746, 1705, 1687, 1598, 1339, 1316, 1253, 1212, 764, 691. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, 1H, J= 6.5 Hz), 7.89-7.86 (m, 3H), 7.81-7.76 (m, 2H), 7.54 (t, 1H, J= 7.3 Hz), 7.44-7.40 (m, 2H), 6.64 (dd, 1H, J_1= 5.4 Hz, J_2= 18.5 Hz), 5.49 (dd, 1H, J_1= 8.2 Hz, J_2= 18.5 Hz), 2.58-2.51 (m, 1H), 2.10 (dd, 1H, J_1= 3.7 Hz, J_2= 8.6 Hz), 1.78 (dd, 1H, J_1= 3.7 Hz, J_2= 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.7, 198.6, 197.8, 142.3, 141.7, 136.4, 134.8, 134.7, 133.2, 128.6, 127.9, 122.6, 122.3, 38.7, 36.0, 30.8, 24.5. Elemental analysis calculated for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.33; H, 5.10. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column, 90:10 *n*-hexane:2-propanol, 1.0 mL/min, detection at 254 nm; minor enantiomer t_R = 21.1 min, major enantiomer t_R = 17.6 min.

2-(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3c)



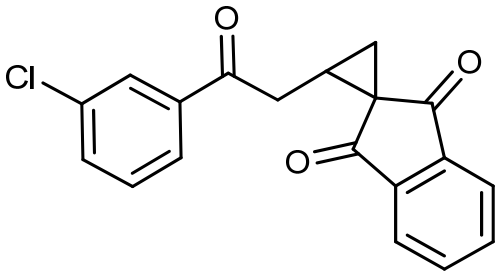
Pale yellow solid, m.p. 93.9-94.9°C. FTIR ν_{max} cm^{-1} 1745, 1707, 1599, 1410, 1325, 1254, 1211, 1170, 1130, 1067, 759. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.98 (m, 2H), 7.88-7.78 (m, 4H), 7.61-7.69 (m, 2H), 3.66 (dd, 1H, J_1= 5.4 Hz, J_2= 18.6 Hz), 3.54 (dd, 1H, J_1= 8.2 Hz, J_2= 18.7 Hz), 2.59-2.51 (m, 1H), 2.12 (dd, 1H, J_1= 4.0 Hz, J_2= 8.7 Hz), 1.78 (dd, J_1= 3.9 Hz, J_2= 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8, 198.4, 197.0, 142.3, 141.7, 139.0, 136.0, 135.2 (q, J= 44 Hz), 134.9, 128.3, 125.7, 125.6, 122.7, 122.4, 38.5, 36.5, 30.2, 24.5. Elemental analysis calculated for $C_{20}H_{13}F_3O_3$: C, 67.04; H, 3.66. Found: C, 67.33; H, 3.82.

2-(2-(4-Chlorophenyl)-2-oxoethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3d)



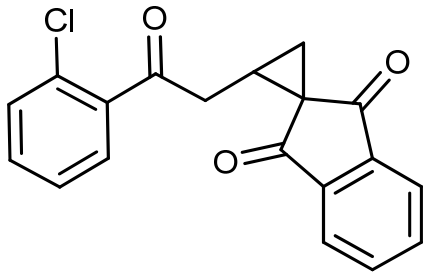
White solid, m.p. 133.5-135.1°C. FTIR ν_{max} cm^{-1} 1738, 1705, 1589, 1400, 1338, 1210, 1092, 992, 819, 762. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, 1H, J= 6.6 Hz), 7.88-7.76 (m, 5H), 7.42-7.40 (m, 2H), 3.61 (dd, 1H, J_1= 5.4 Hz, J_2= 18.6 Hz), 3.49 (dd, 1H, J_1= 8.2 Hz, J_2= 18.5 Hz), 2.57-2.50 (m, 1H), 2.11 (dd, 1H, J_1= 4.2 Hz, J_2= 8.6 Hz), 1.78 (dd, J_1= 3.9 Hz, J_2= 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8, 198.5, 196.6, 142.3, 141.7, 139.7, 134.9, 134.8, 129.3, 128.9, 122.6, 122.4, 38.6, 36.1, 30.5, 24.5. Elemental analysis calculated for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 70.37; H, 4.08.

2-(2-(3-Chlorophenyl)-2-oxoethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3e)



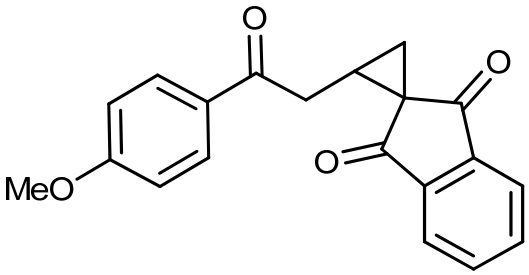
Pale yellow solid, m.p. 131.8-134.0°C. FTIR ν_{max} cm^{-1} 1748, 1704, 1598, 1339, 1255, 1208, 766. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.98 (m, 1H), 7.89-7.76 (m, 5H), 7.54-7.51 (m, 1H), 7.40-7.37 (m, 1H), 3.62 (dd, 1H, J_1= 5.4 Hz, J_2= 18.6 Hz), 3.48 (dd, 1H, J_1= 8.3 Hz, J_2= 18.6 Hz), 2.55-2.53 (m, 1H), 2.11 (dd, 1H, J_1= 3.9 Hz, J_2= 8.7 Hz), 1.78 (dd, J_1= 3.9 Hz, J_2= 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ. 198.8, 198.5, 196.6, 142.3, 141.8, 137.9, 134.8, 133.2, 130.0, 128.1, 126.0, 122.7, 122.4, 38.6, 36.3, 30.4, 24.5. Elemental analysis calculated for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 70.45; H, 4.14.

2-(2-(2-Chlorophenyl)-2-oxoethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3f)



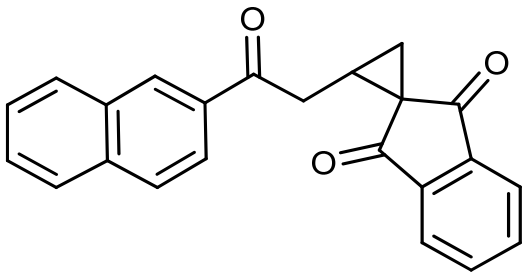
Pale yellow solid, m.p. 80.6-83.8°C. FTIR ν_{max} cm^{-1} 1739, 1706, 1598, 1469, 1433, 1340, 1253, 1209, 761. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.99-7.96 (m, 1H), 7.90-7.86 (m, 1H), 7.85-7.78 (m, 2H), 7.41-7.38 (m, 1H), 7.36-7.31 (m, 2H), 7.28-7.24 (m, 1H), 3.59 (dd, 1H, J_1= 5.3 Hz, J_2= 18.6 Hz), 3.44 (dd, 1H, J_1= 8.6 Hz, J_2= 18.6 Hz), 2.52-2.48 (m, 1H), 2.08 (dd, 1H, J_1= 3.9 Hz, J_2= 8.7 Hz), 1.77 (dd, 1H, J_1= 3.9 Hz, J_2= 8.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.9, 198.6, 198.5, 142.4, 141.7, 138.6, 134.7, 131.8, 130.5, 128.8, 126.9, 122.6, 122.4, 40.4, 38.6, 30.7, 24.3. Elemental analysis calculated for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03; Found: C, 70.55; H, 4.38.

2-(2-(4-Methoxyphenyl)-2-oxoethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3g)



Pale yellow solid, m.p. 144.2-147.3°C. FTIR ν_{max} cm^{-1} 1738, 1705, 1678, 1600, 1338, 1221, 1171, 757. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99-7.97 (m, 1H), 7.88-7.86 (m, 3H), 7.82-7.75 (m, 2H), 6.90 (d, 1H, J= 8.8 Hz), 3.85 (s, 3H), 3.59 (dd, 1H, J_1= 5.6 Hz, J_2= 18.2 Hz), 3.43 (dd, 1H, J_1= 8.2 Hz, J_2= 18.2 Hz), 2.59-2.51 (m, 1H), 2.10 (dd, 1H, J_1= 3.8 Hz, J_2= 8.7 Hz), 1.78 (dd, J_1= 3.8 Hz, J_2= 8.2 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8, 198.7, 196.3, 163.6, 142.4, 141.8, 134.7, 134.6, 130.2, 129.6, 122.6, 122.3, 113.7, 55.5, 38.8, 35.6, 31.2, 24.6. Elemental analysis calculated for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03; Found: C, 75.25; H, 5.27.

2-(2-(Naphthalen-2-yl)-2-oxoethyl)spiro[cyclopropane-1,2'-indene]-1',3'-dione (3h)



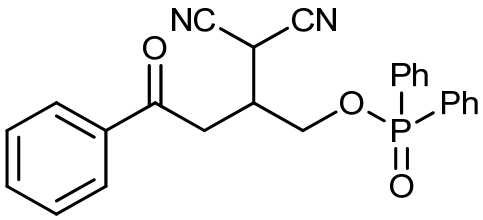
Pale yellow solid, m.p. 142.1-143.9°C. FTIR ν_{max} cm^{-1} 2924, 2854, 1746, 1705, 1682, 1597, 1468, 1338, 1253, 1210, 755. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (bs, 1H), 7.98-7.77 (m, 8H), 7.61-7.52 (m, 2H), 3.78 (dd, 1H, J_1= 5.2 Hz, J_2= 18.2 Hz), 3.63 (dd, 1H, J_1= 7.9 Hz, J_2= 18.0 Hz), 2.64-2.60 (m, 1H), 2.14 (bd, 1H), 1.83 (bd, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8, 198.6, 197.4, 142.4, 141.8, 134.8, 134.7, 133.8, 132.5, 129.7, 129.6, 128.5, 127.7, 126.8, 123.6, 122.6, 122.4, 38.8, 36.1, 31.02, 24.6. Elemental analysis calculated for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74; Found: C, 81.33; H, 4.90.

Synthesis of Michael adduct 5

Diphenylphosphinate **1a** (0.10 mmol), malononitrile (7.3 mg, 0.11 mmol) and K_2CO_3 (14 mg, 0.10 mmol) were mixed in dry $CHCl_3$ (2.0 mL). The reaction mixture was stirred at room temperature

for 21 h, then it was directly purified by flash chromatography (eluent from PE/ ethyl acetate 8:2 to 6:4) to give product **5** (50% yield).

2-(Dicyanomethyl)-4-oxo-4-phenylbutyl diphenylphosphinate (5)

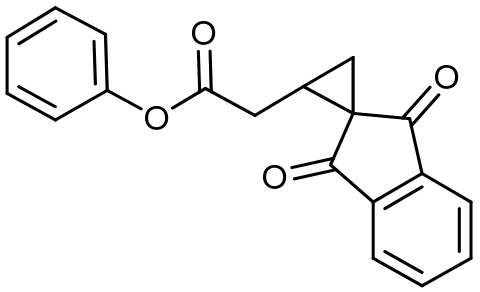


White wax. FTIR ν_{max} cm^{-1} 2922, 2852, 2255, 1719, 1685, 1596, 1466, 1439, 1220, 1025, 730, 694, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.80 (m, 5H), 7.64-7.43 (m, 10H), 4.67 (d, 1 H, J= 5.6 Hz), 4.36-4.30 (m, 1H), 4.26-4.20 (m, 1H), 3.45 (dd, 1H, J_1= 6.5 Hz, J_2= 18.5 Hz), 3.35 (3.20-3.13 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.1, 135.6, 134.2, 132.8, 132.1, 131.8, 131.7, 131.6, 131.5, 128.9, 128.8 (d, J= 3 Hz), 128.6, 128.4, 128.2, 111.7, 111.6, 63.9 (d, J= 5 Hz), 36.9, (d, J= 6 Hz), 36.6, 24.5. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.6 (s). Elemental analysis calculated for $C_{25}H_{21}N_2O_3P$: C, 70.09; H, 4.94; Found: C, 70.32; H, 4.98.

Baeyer-Villiger oxidation of cyclopropane 3b

In a sample vial cyclopropane **3b** (29 mg, 0.10 mmol) and crystallized *m*-CPBA (35 mg, 0.20 mmol) was dissolved in 1 mL of dichloromethane and heated at 55°C for 3 days. Then a second addiction of *m*-CPBA (0.20 mmol) was performed, and stirring continued for 2 days, until compound **3b** disappeared as monitored by ^{1}H NMR analysis (ketone and ester have the same mobility on TLC). Direct purification by flash chromatography (eluent EP/ AcOEt 9:1) gave cyclopropane ester **4a** in 84% yield.

Phenyl 2-(1',3'-dioxo-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-2-yl)acetate (4a)



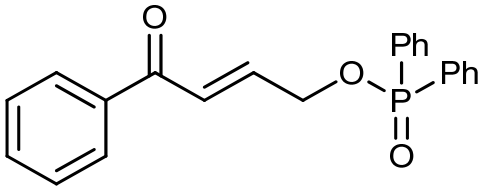
White solid, m.p. 80.0-82.5°C. FTIR ν_{max} cm^{-1} 1758, 1706, 1597, 1339, 1310, 1197, 1146, 748. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.93 (m, 2H), 7.79-7.77 (m, 2H), 7.45-7.41 (m, 1H), 7.32-7.28 (m,

1H), 7.18-7.14 (m, 1H), 6.95-6.93 (m, 2H), 3.21 (dd, 1H, J_1= 5.7 Hz, J_2= 17.6 Hz), 3.11 (dd, 1H, J_1= 8.9 Hz, J_2= 17.6 Hz), 2.54-2.47 (m, 1H), 2.08 (dd, 1H, J_1= 4.0 Hz, J_2= 8.7 Hz), 1.83 (dd, J_1= 4.0 Hz, J_2= 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.4, 198.3, 170.2, 150.4, 142.4, 141.6, 134.9, 133.8, 129.8, 129.3, 128.3, 125.8, 122.5, 121.3, 38.5, 31.8, 30.6, 24.3. Elemental analysis calculated for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61; Found: C, 74.83; H, 4.84.

General procedure for the synthesis of compounds 1

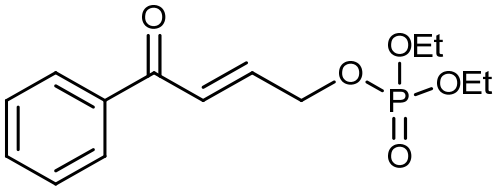
To a solution of freshly synthetized hydroxy-enones[2] (2.0 mmol) in anhydrous CH_2Cl_2 (4 mL), pyridine (388 μL, 4.8 mmol) and 4-(dimethylamino)pyridine (12.2 mg, 0.10 mmol) were added at 0°C, followed by diphenylphosphinic chloride (572 μL, 3.0 mmol). The reaction was warmed at room temperature and stirred overnight. Then, the mixture was poured in water, and few drops of saturated aqueous solution of Na_2CO_3 were added. The aqueous phase was extracted twice with chloroform. Collected organic phases were dried over Na_2SO_4, and the solvent removed under reduced pressure. Purification of the crude mixture with flash chromatography (eluent from EP/AcOEt 8:2 to 1:1) gave diphenylphosphinates **1** (yields ranging from 51 to 80%).

(*E*)-4-Oxo-4-phenylbut-2-en-1-yl diphenylphosphinate (1a)



White solid, m.p. 77.3-79.8°C. FTIR ν_{max} cm^{-1} 1676, 1629, 1596, 1439, 1284, 1131, 730, 695, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.85 (m, 5H), 7.83-7.47 (m, 10H), 7.21-7.18 (m, 1H), 7.04-7.00 (m, 1H), 4.82 (bs, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.9, 141.6 (d, J= 7 Hz), 137.2, 133.0, 132.4, 132.0, 131.9, 131.8, 131.6, 131.5, 130.1, 128.7, 128.5, 125.8, 63.4 (d, J= 5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.3 (s). Elemental analysis calculated for $C_{22}H_{19}O_3P$: C, 74.50; H, 4.61; Found: C, 74.92; H, 5.69.

(*E*)-Diethyl (4-oxo-4-phenylbut-2-en-1-yl) phosphate (1b)

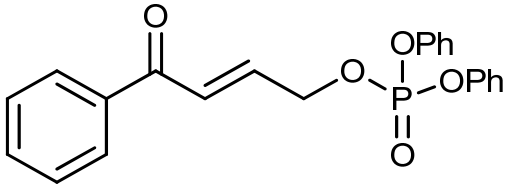


Pale yellow oil. IR ν_{max} (KBr)/cm^{-1} 2926, 1678, 1632, 1449, 1270, 1035, 977, 694. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.86 (m, 1H), 7.51-7.47 (m, 1H), 7.41-7.37 (m, 2H), 7.17-7.12 (m, 1H), 7.13-7.12 (m, 1H), 6.96-6.90 (m, 1H), 4.75-4.72 (m, 2H), 4.12-3.98 (m, 4H), 1.30-1.23 (m, 6H). ^{13}C

[2] The corresponding hydroxy-enones were synthetized as reported in the literature. See: (a) B. W. Greatrex, M. C. Kimber, D. K. Taylor and E. R. T. Tiekink, *J. Org. Chem.* **2003**, *68*, 4239; (b) T. Inokuma, K. Takasu, T. Sakaeda and Y. Takemoto, *Org. Lett.* **2009**, *11*, 2425.

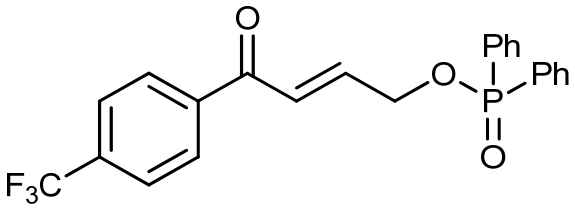
NMR ($CDCl_3$, 100 MHz): δ. 189.5, 141.0 (d, J= 7Hz), 137.1, 133.0, 128.4, 128.5, 128.4, 125.2, 65.8 (d, J= 5 Hz), 63.9 (d, J= 6 Hz), 63.4 (d, J= 6 Hz), 16.0 (t, J= 3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ -0.93 (s). Elemental analysis calculated for $C_{14}H_{19}O_5P$: C, 56.37; H, 6.42; Found: C, 56.50; H, 6.70.

(*E*)-4-Oxo-4-phenylbut-2-en-1-yl diphenyl phosphate (1c)



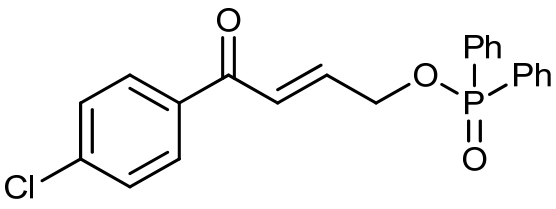
White solid, m.p. 42.1-43.0°C. FTIR ν_{max} cm^{-1} 1678, 1632, 1591, 1448, 1293, 1190, 958, 755, 689. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.85 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 7.38-7.34 (m, 4H), 7.27-7.25 (m, 4H), 7.23-7.19 (m, 2H), 7.17-7.12 (m, 1H), 7.03-7.97 (m, 1H), 5.04-5.01 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.4, 150.4 (d, J= 8 Hz), 140.0 (d, J= 8 Hz), 137.1, 133.2, 130.0, 128.6, 125.6 (d, J= 6Hz), 120.0 (d, J= 5 Hz), 67.3 (J= 5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ -11.9 (s). Elemental analysis calculated for $C_{22}H_{19}O_5P$: C, 67.00; H, 4.86; Found: C, 67.40; H, 4.88.

(*E*)-4-Oxo-4-(4-(trifluoromethyl)phenyl)but-2-en-1-yl diphenylphosphinate (1d)



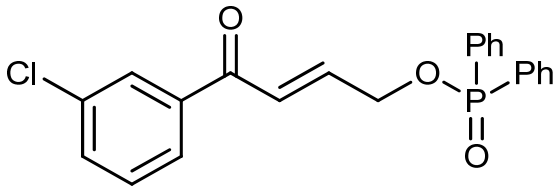
Pale yellow wax. FTIR ν_{max} cm^{-1} 1679, 1633, 1440, 1322, 1228, 1170, 1131, 1067, 1016, 754, 730, 697, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.91 (m, 2H), 7.86-7.76 (m, 4H), 7.68-7.63 (m, 2H), 7.54-7.41 (m, 6H), 7.17-7.11 (m, 1H), 7.06-7.00 (m, 1H), 4.82-4.79 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.9, 143.1 (d, J= 6 Hz), 140.0, 132.4, 131.9, 131.5, 131.4, 130.0, 128.8, 128.7, 128.6, 128.4, 128.3, 125.5, 125.2, 63.3 (d, J= 5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.4 (s). Elemental analysis calculated for $C_{23}H_{18}F_3O_3P$: C, 64.19; H, 4.22; Found: C, 64.52; H, 4.40.

(*E*)-4-(4-Chlorophenyl)-4-oxobut-2-en-1-yl diphenylphosphinate (1e)



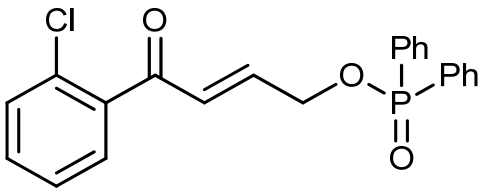
Pale yellow wax. FTIR ν_{max} cm^{-1} 1675, 1630, 1588, 1439, 1291, 1227, 1131, 1091, 1013, 730, 687, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.78 (m, 6H), 7.57-7.53 (m, 2H), 7.50-7.41 (m, 6H), 7.14-7.12 (m, 1H), 7.05-7.00 (m, 1H), 4.83-4.80 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.6, 142.2 (d, J= 7 Hz), 139.5, 135.6, 132.5, 132.4, 132.3, 132.0, 131.6, 131.5, 131.4, 130.1, 130.0, 129.7, 128.9, 128.8, 128.6, 128.5, 128.4, 125.3, 63.5 (d, J= 5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.4 (s). Elemental analysis calculated for $C_{22}H_{18}ClO_3P$: C, 66.59; H, 4.57; Found: C, 66.62; H, 4.63.

(*E*)-4-(3-Chlorophenyl)-4-oxobut-2-en-1-yl diphenylphosphinate (1f)



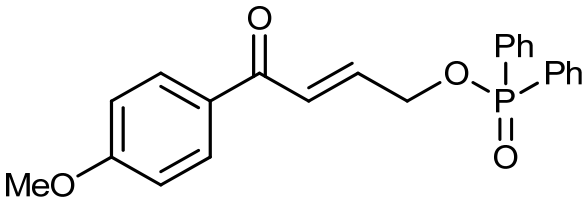
Pale yellow wax. FTIR ν_{max} cm^{-1} 1678, 1634, 1439, 1227, 1131, 1024, 730, 696, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.75 (m, 6H), 7.59-7.39 (m, 8H), 7.15-7.12 (m, 1H), 7.07-7.01 (m, 1H), 4.84-4.82 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.7, 142.7 (d, J= 6 Hz), 138.9, 135.0, 133.0, 132.6, 132.1, 131.7, 131.6, 131.5, 130.0, 128.8, 128.7, 128.6, 126.7, 125.3, 63.4 (d, J= 5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.4 (s). Elemental analysis calculated for $C_{22}H_{18}ClO_3P$: C, 66.59; H, 4.57; Found: C, 66.61; H, 4.60.

(*E*)-4-(2-Chlorophenyl)-4-oxobut-2-en-1-yl diphenylphosphinate (1g)



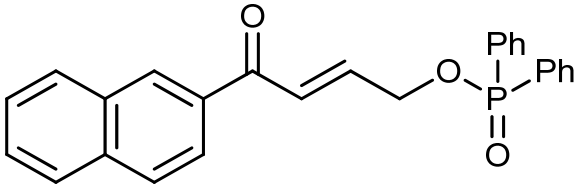
Brown gum. FTIR ν_{max} cm^{-1} 1687, 1591, 1467, 1439, 1378, 1227, 1131, 958, 730, 696, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.69 (m, 4H), 7.47-7.15 (m, 10H), 6.82-6.78 (m, 1H), 6.71-6.65 (m, 1H), 4.73-4.69 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.8, 144.5 (d, J= 7 Hz), 132.3, 132.1, 131.9, 131.8, 131.4, 131.3, 130.8, 130.6, 130.1, 129.7, 129.6, 129.2, 129.1, 128.6, 128.4, 128.3, 128.2, 126.9, 126.7, 62.7 (d, J= 4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.4 (s). Elemental analysis calculated for $C_{22}H_{18}ClO_3P$: C, 66.59; H, 4.57; Found: C, 66.92; H, 4.72.

(*E*)-4-(4-Methoxyphenyl)-4-oxobut-2-en-1-yl diphenylphosphinate (1h)



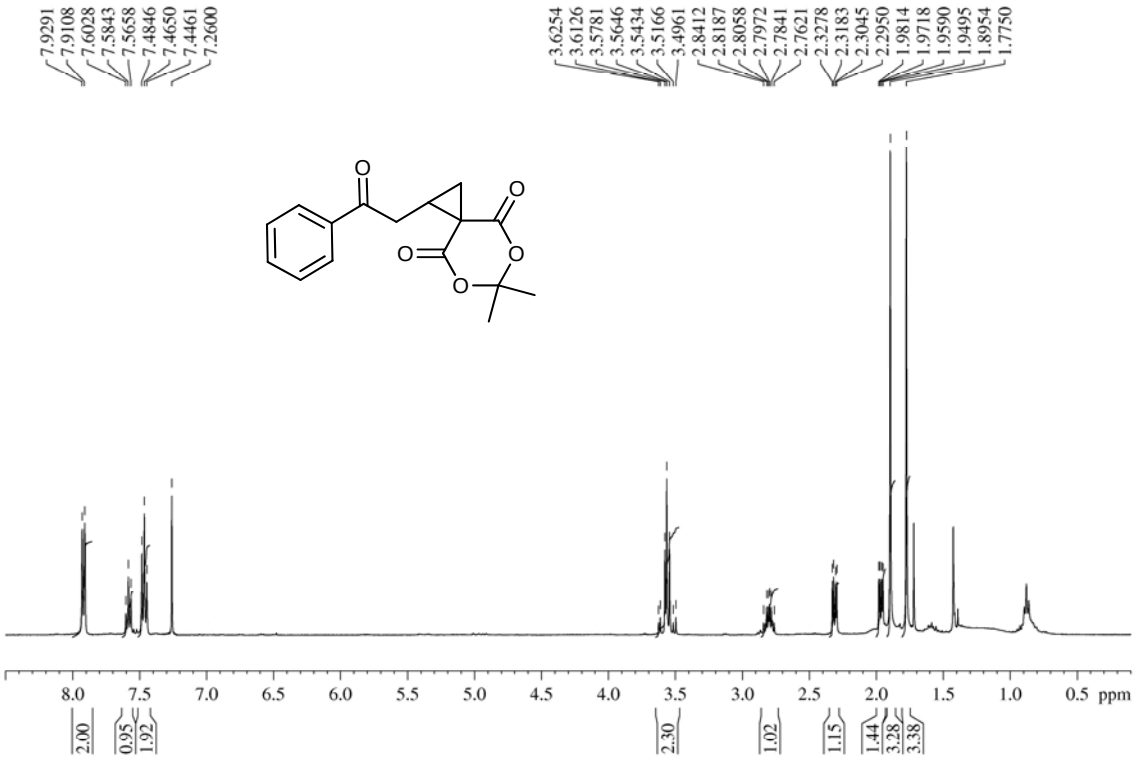
White solid, m.p. 102.0-103.1°C. FTIR ν_{max} cm^{-1} 1671, 1627, 1598, 1439, 1260, 1227, 1172, 1131, 1023, 730, 698, 560. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92-7.83 (m, 6H), 7.57-7.45 (m, 6H), 2.22-2.17 (m, 6H), 7.22-7.17 (m, 1H), 7.03-6.97 (m, 1H), 4.82-4.79 (m, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ. 188.2, 163.6, 140.7 (d, J= 8 Hz), 132.5, 131.6, 131.5, 131.0, 130.2, 128.7, 128.6, 125.7, 113.8, 63.6 (d, J= 5 Hz), 55.5. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 33.1 (s). Elemental analysis calculated for $C_{23}H_{21}O_4P$: C, 70.40; H, 5.39; Found: C, 70.72; H, 5.62.

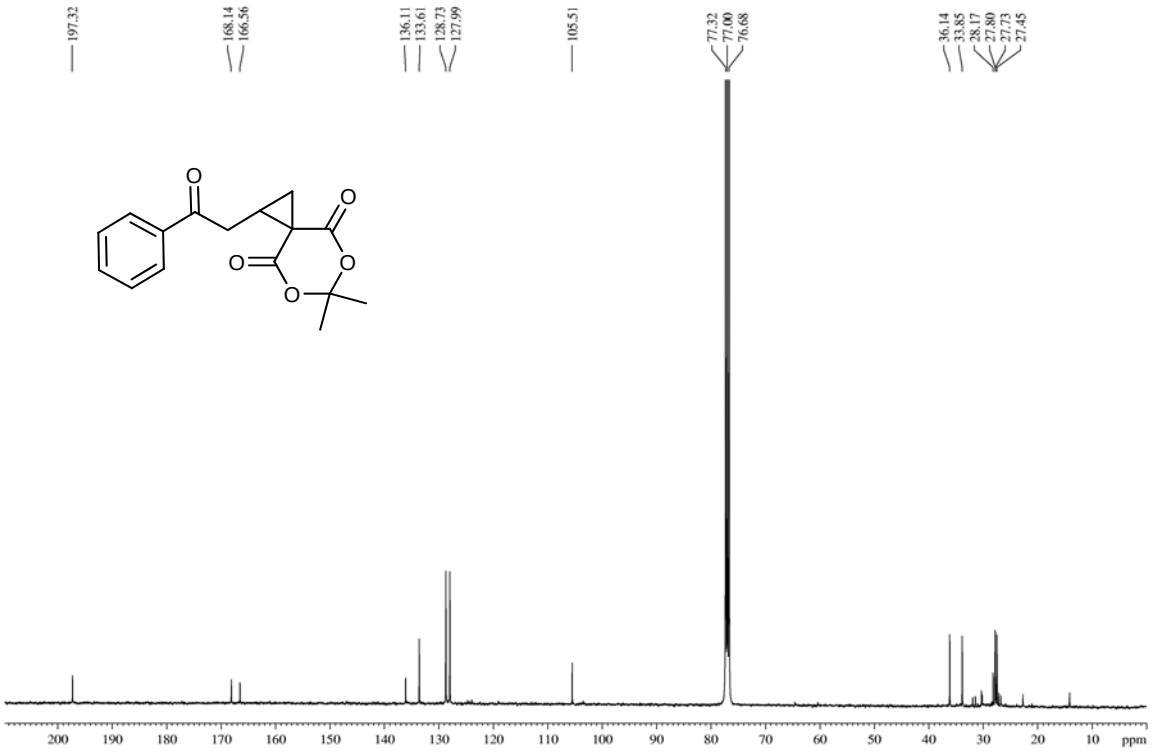
(*E*)-4-(Naphthalen-2-yl)-4-oxobut-2-en-1-yl diphenylphosphinate (1i)

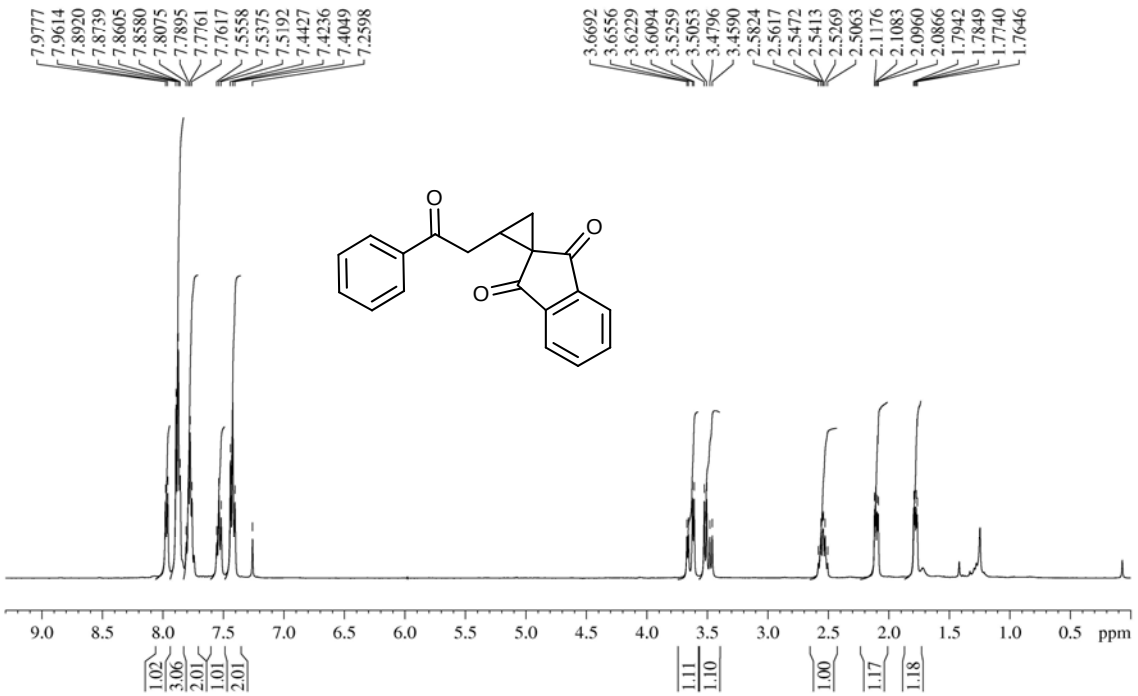


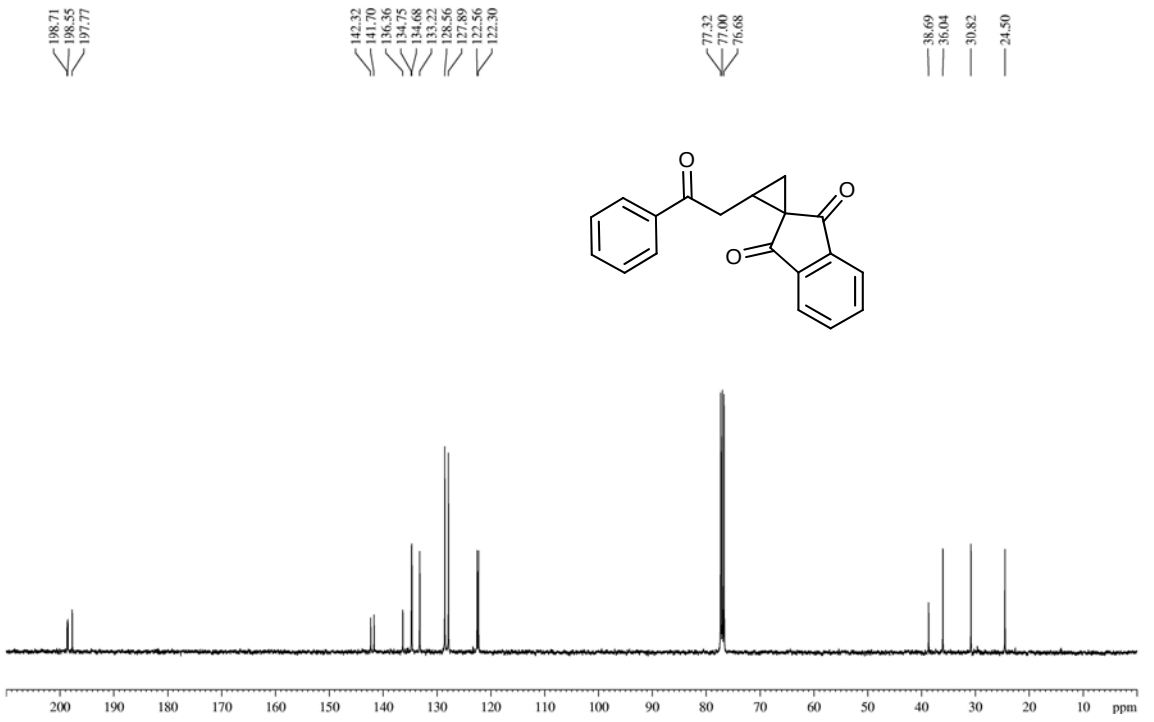
Pale yellow wax. FTIR ν_{max} cm^{-1} 2926, 1673, 1626, 1592, 1439, 1289, 1226, 1131, 1033, 955, 752, 730, 697, 561, 534. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (bs, 1H), 7.98-7.77 (m, 6H), 7.56-7.40 (m, 7H), 7.34-7.26 (m, 1H), 7.08-7.04 (m, 1H), 4.83 (bd 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.6, 141.4, 135.4, 134.6, 132.4, 132.0, 131.6, 131.5, 131.4, 130.9, 130.2, 129.4, 128.7, 128.6, 128.4, 128.3, 127.7, 126.7, 126.0, 124.2, 63.5 (d, J= 5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.4 (s). Elemental analysis calculated for $C_{26}H_{21}O_3P$: C, 75.72; H, 5.13; Found: C, 75.90; H, 5.20.

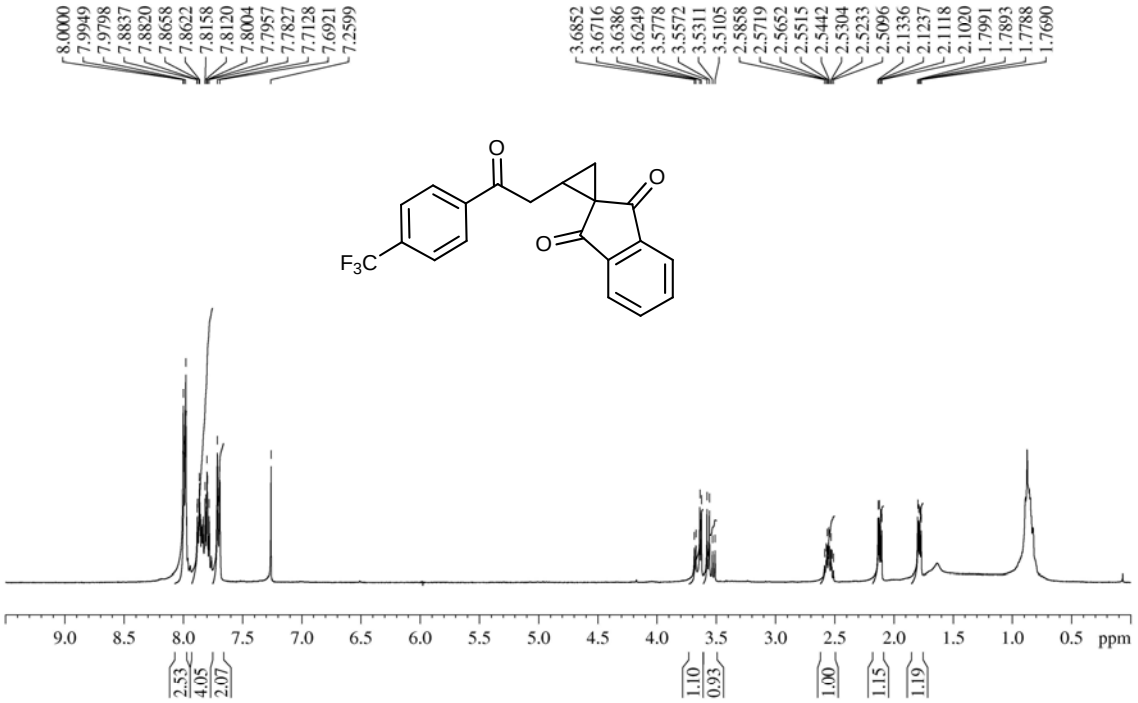
^{1}H NMR and ^{13}C NMR spectra







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7.7957
7.7827
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7.6921
7.2599
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3.6716
3.6386
3.6249
3.5778
3.5572
3.5311
3.5105
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2.5719
2.5652
2.5515
2.5442
2.5304
2.5233
2.5096
2.1336
2.1237
2.1118
2.1020
1.7991
1.7893
1.7788
1.7690
O
O
O
F3C
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1.10
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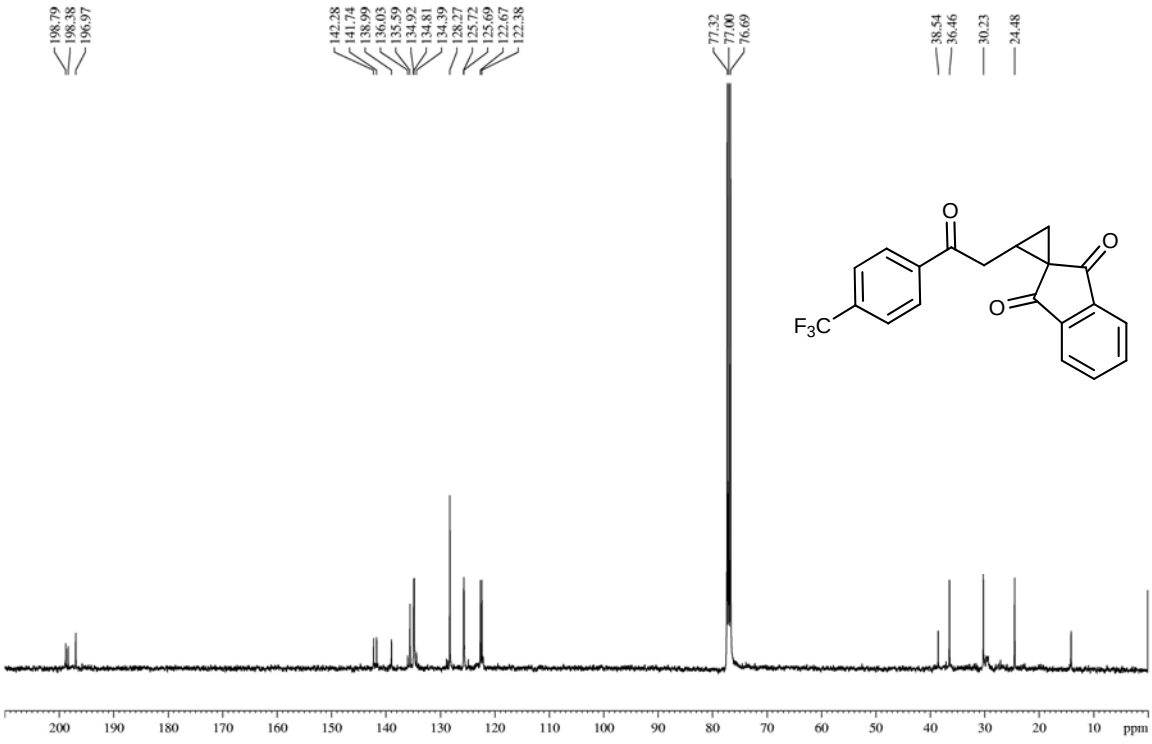
1.15
1.19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136.03
135.59
134.92
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134.39
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125.69
122.67
122.38
77.32
77.00
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O
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O
F3C
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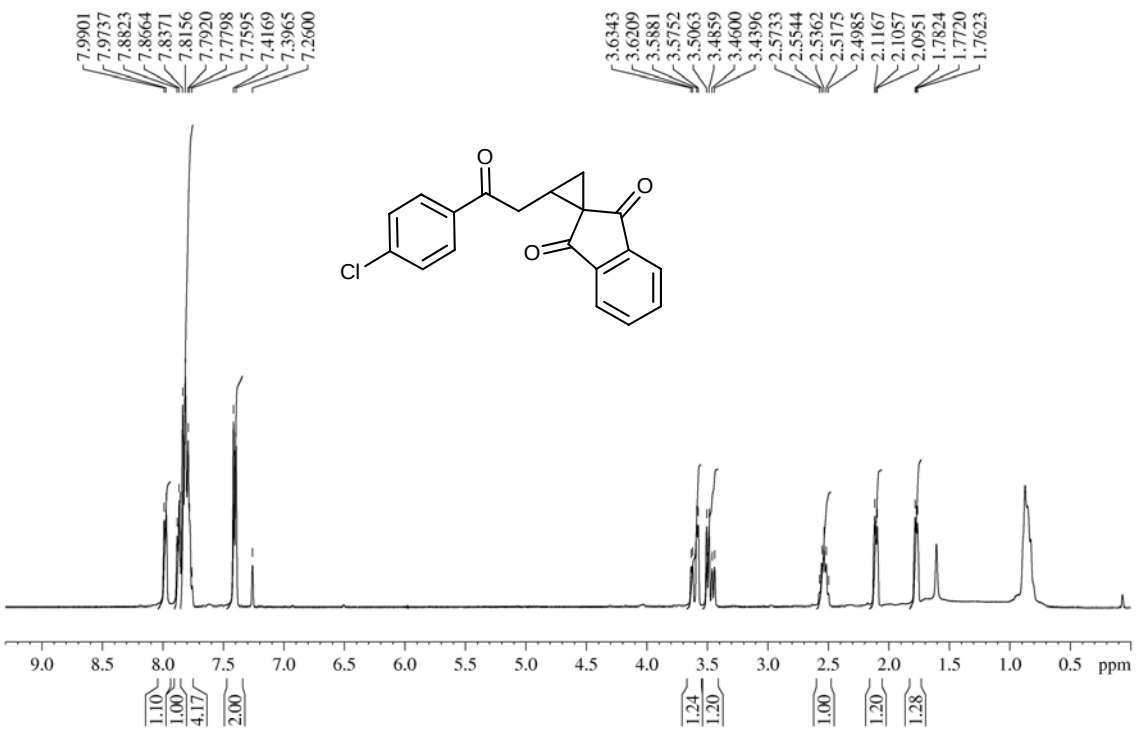

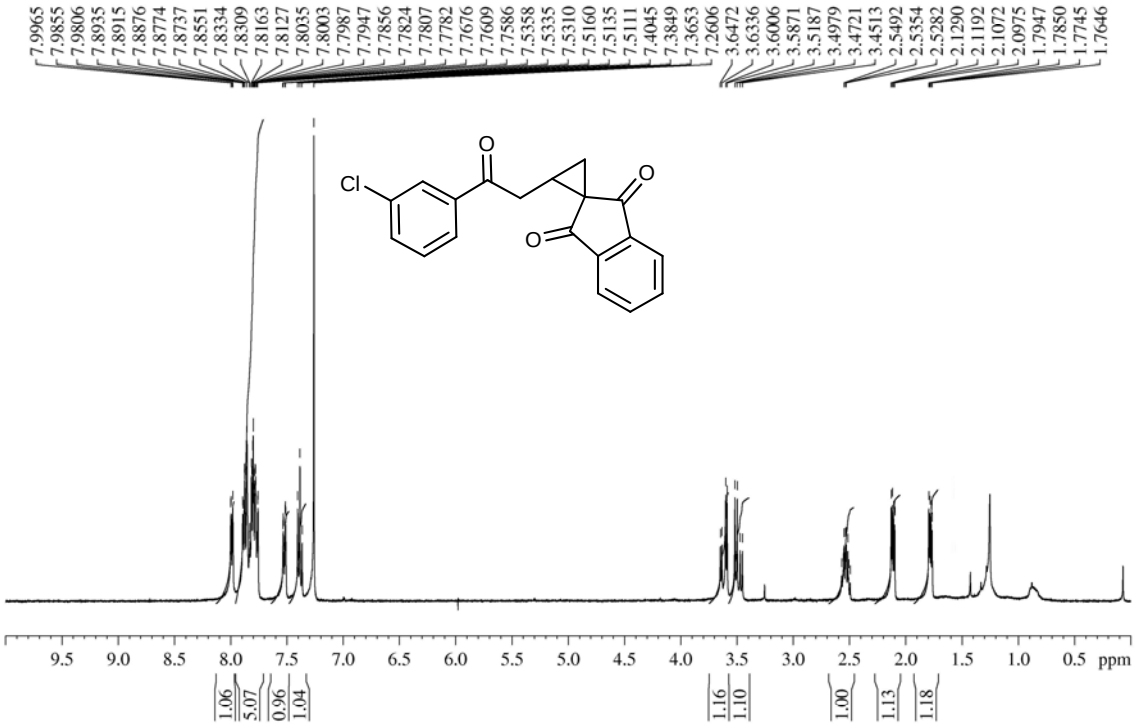
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2.1192
2.1072
2.0975
1.7947
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1.7745
1.7646
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O
O
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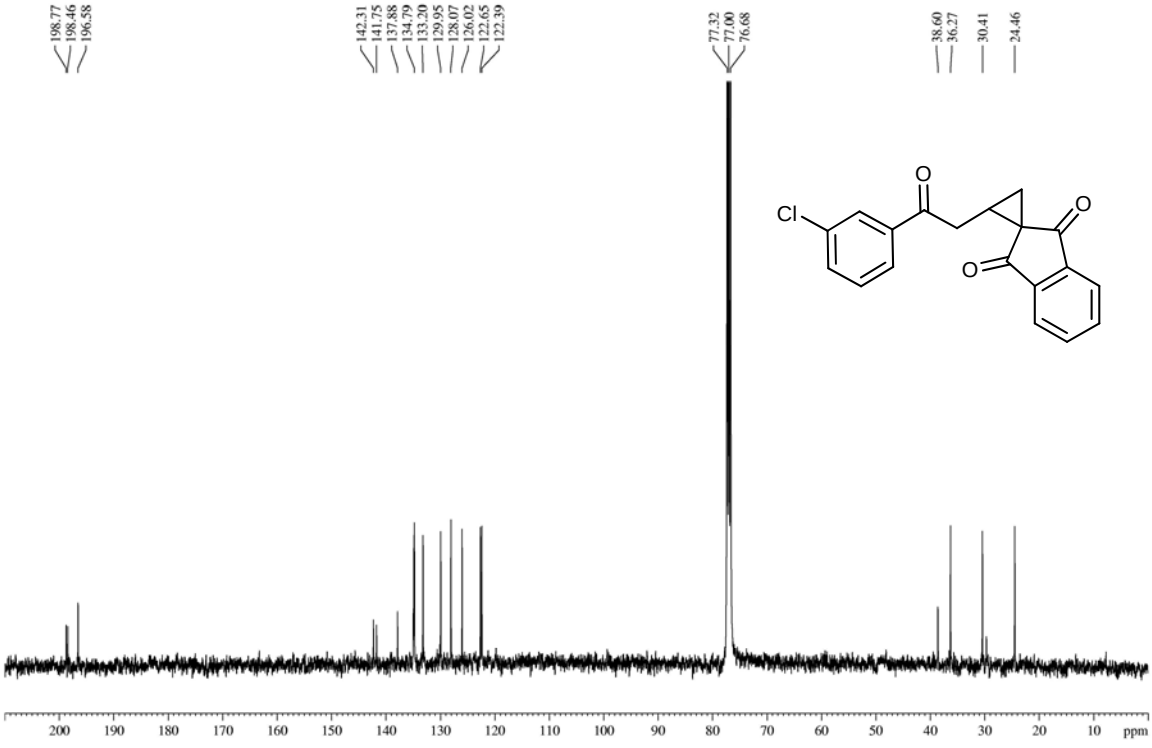
1.13
1.18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77.32
77.00
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36.27
30.41
24.46
Cl
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O
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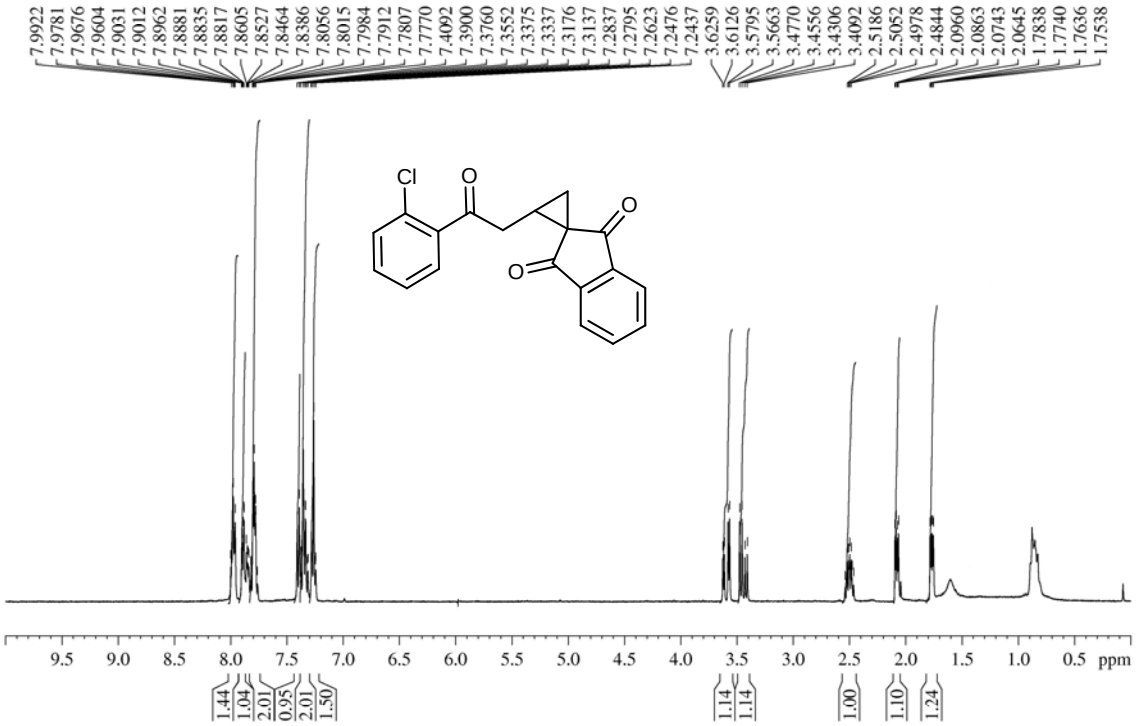
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1.7740
1.7636
1.7538
Cl
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O
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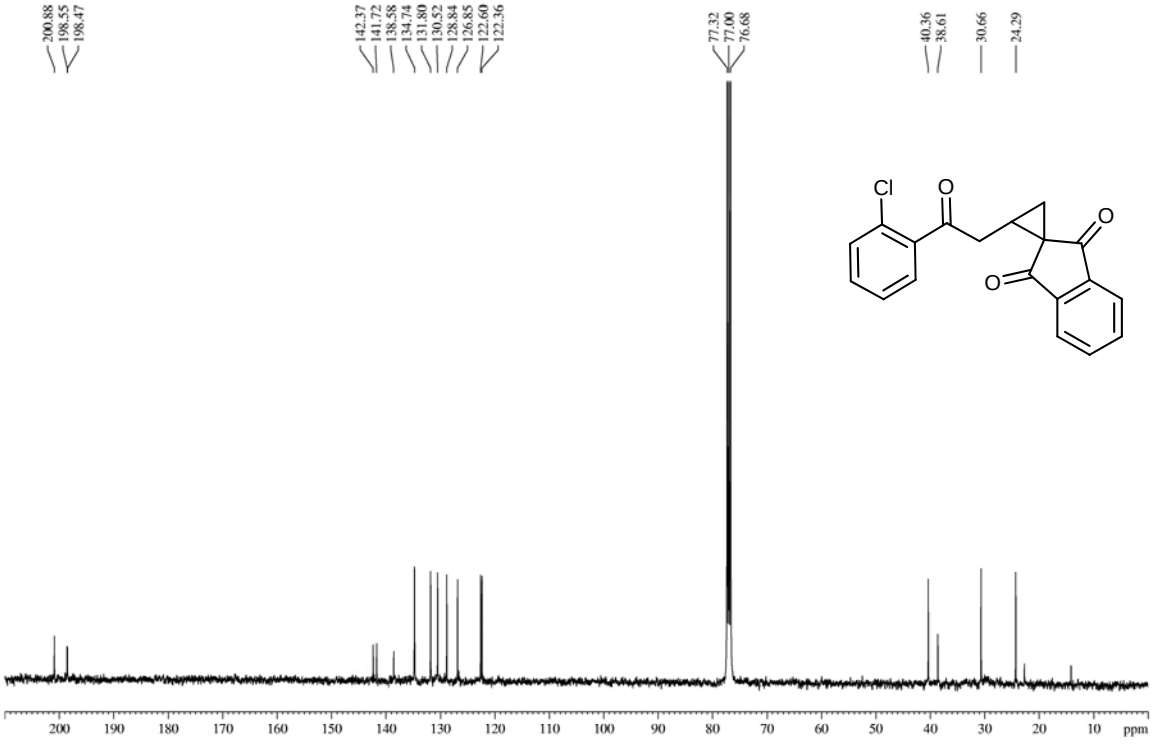
1.00
1.10
1.24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138.58
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122.36
77.32
77.00
76.68
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38.61
30.66
24.29
Cl
O
O
O
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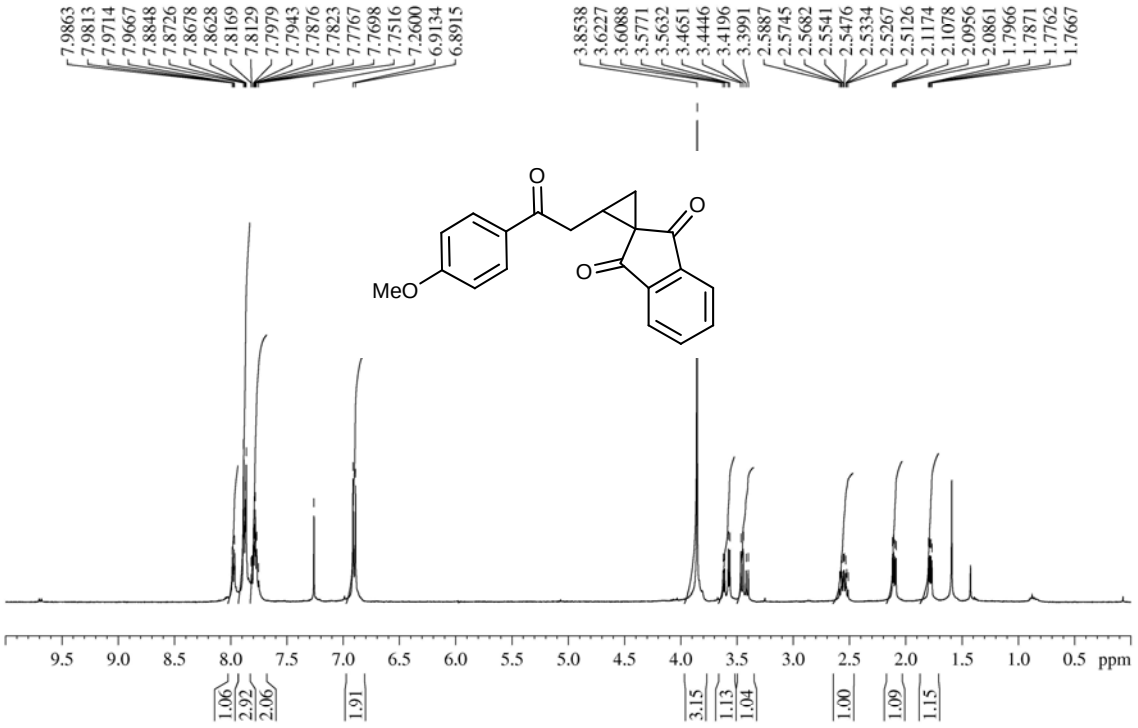
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O
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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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1.13
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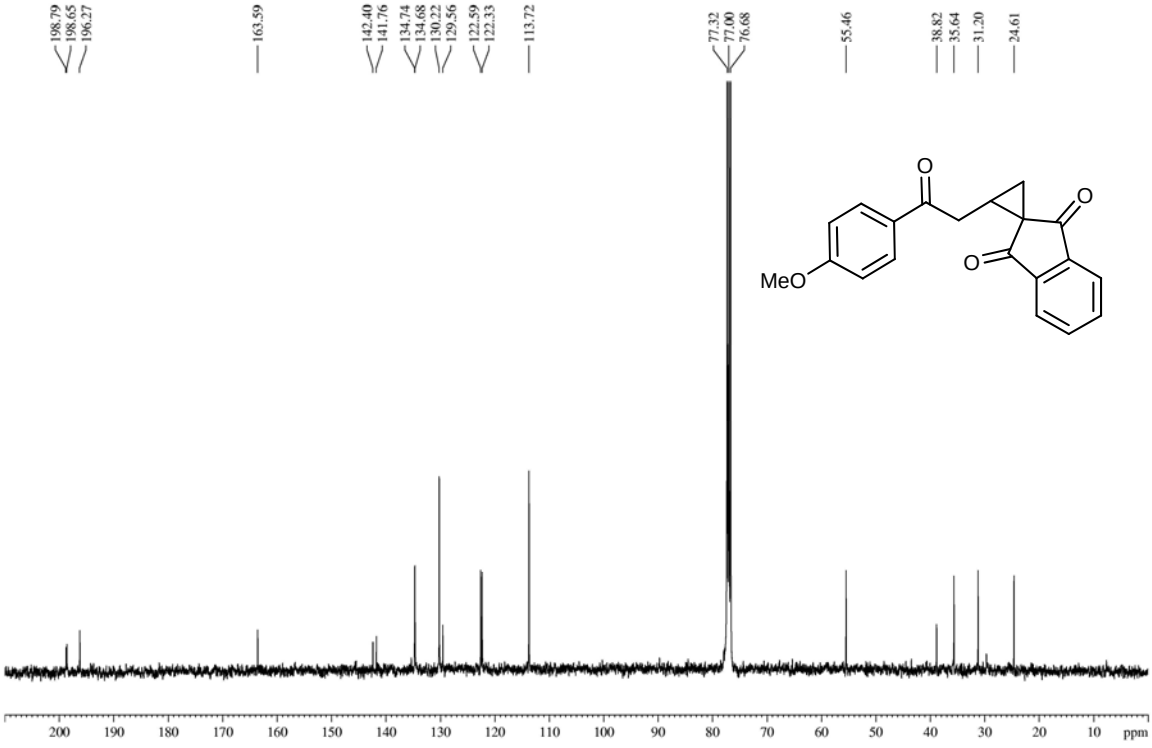
1.15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113.72
77.32
77.00
76.68
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31.20
24.61
MeO
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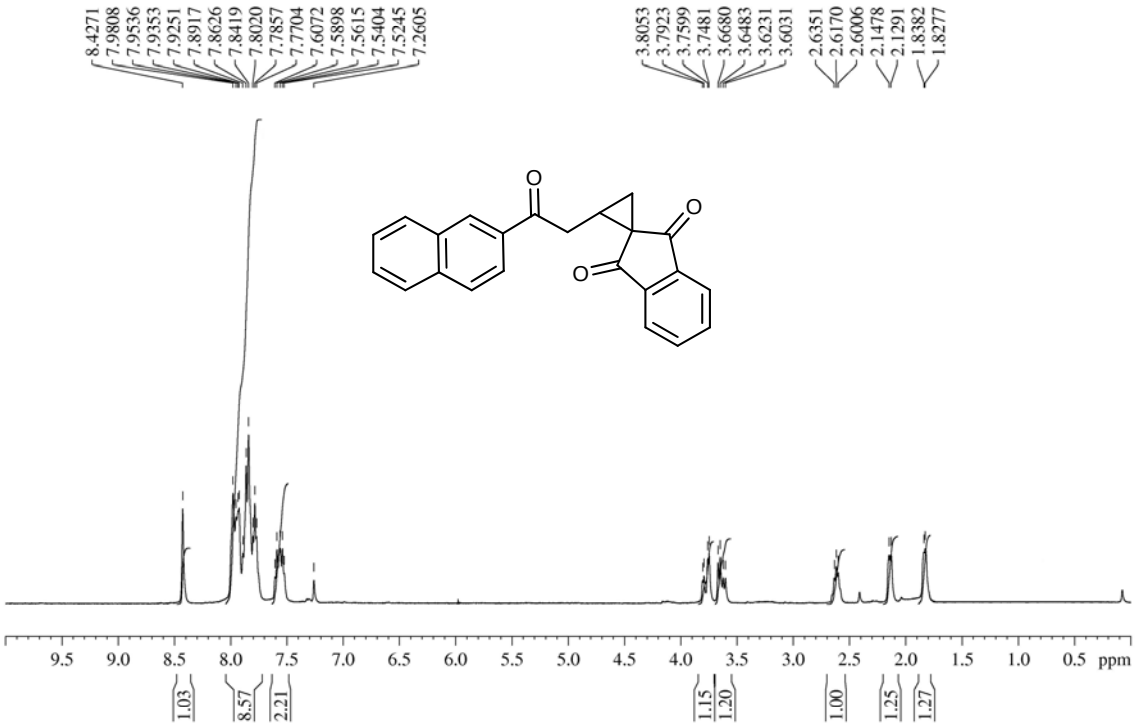
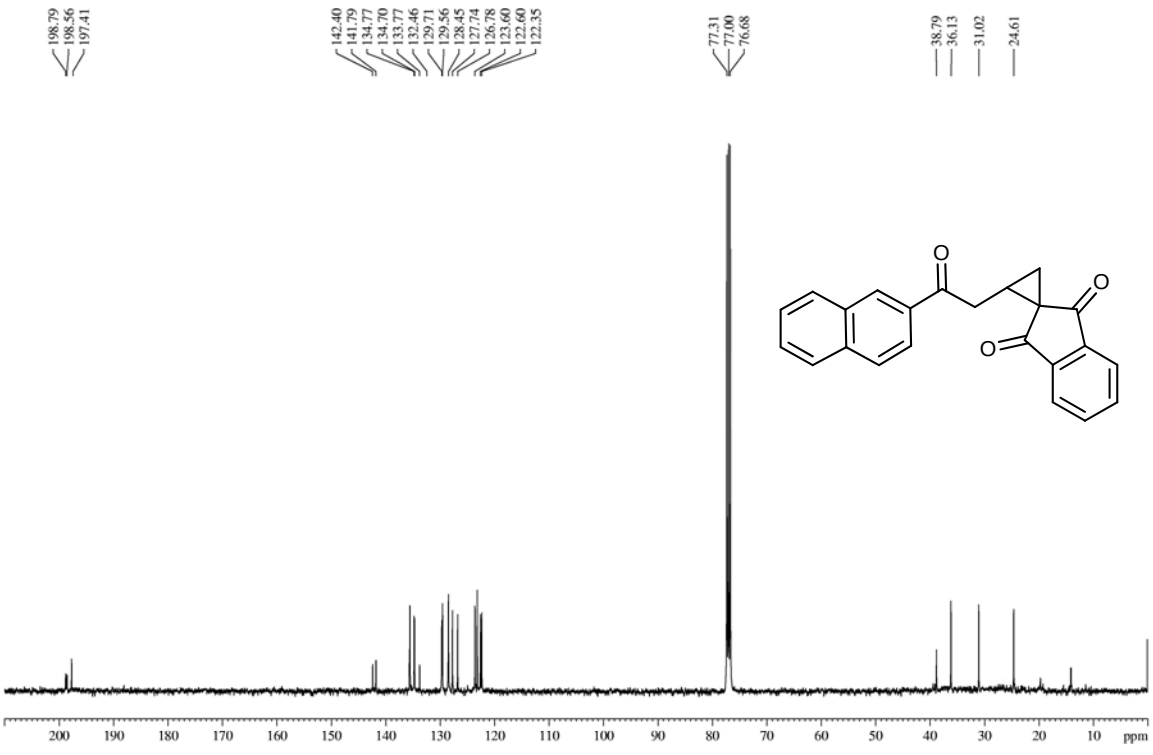
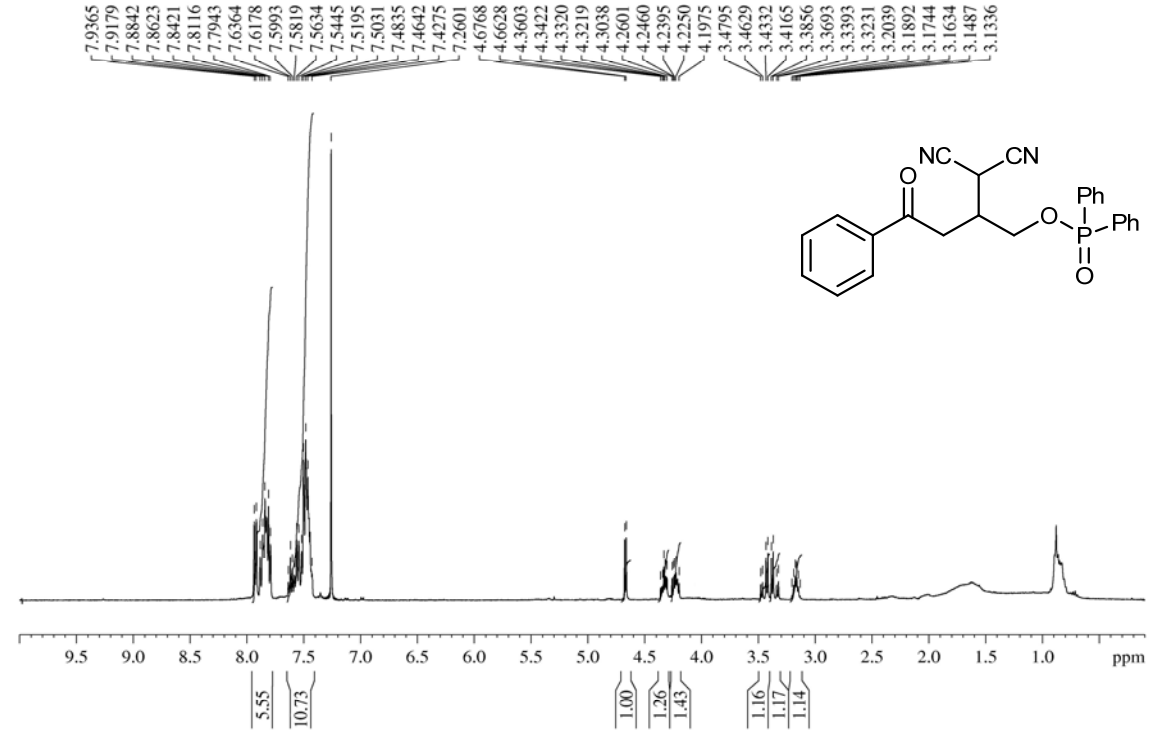
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



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7.5445
7.5195
7.5031
7.4835
7.4642
7.4275
7.2601
4.6768
4.6628
4.3603
4.3422
4.3320
4.3219
4.3038
4.2601
4.2460
4.2395
4.2250
4.1975
3.4795
3.4629
3.4332
3.4165
3.3856
3.3693
3.3393
3.3231
3.2039
3.1892
3.1744
3.1634
3.1487
3.1336
NC
CN
O
Ph
O
P
Ph
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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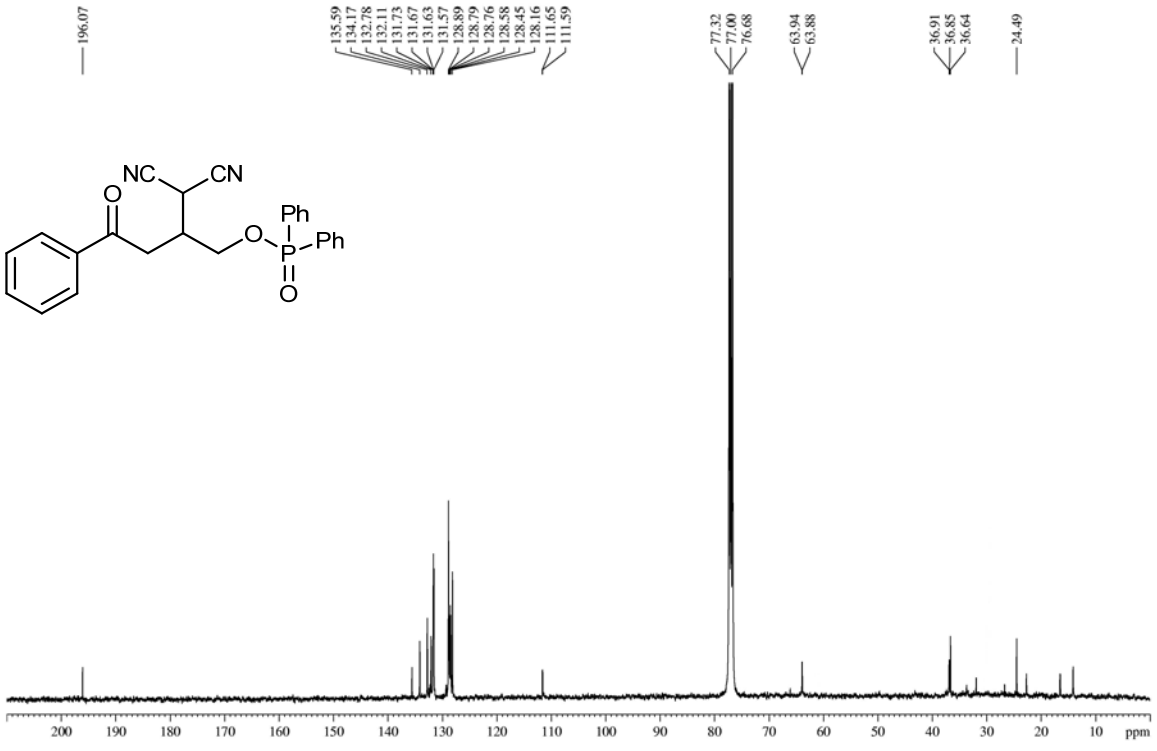
10.73
1.00
1.26
1.43
1.16
1.17
1.14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135.59
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131.73
131.67
131.63
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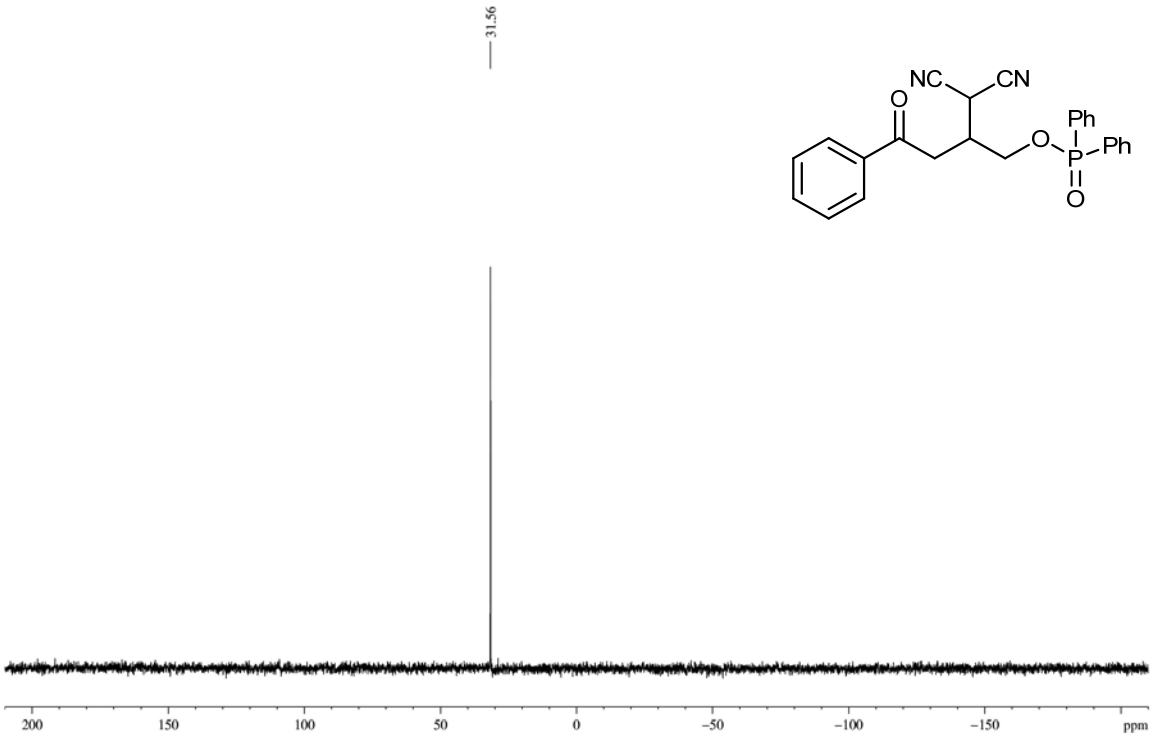
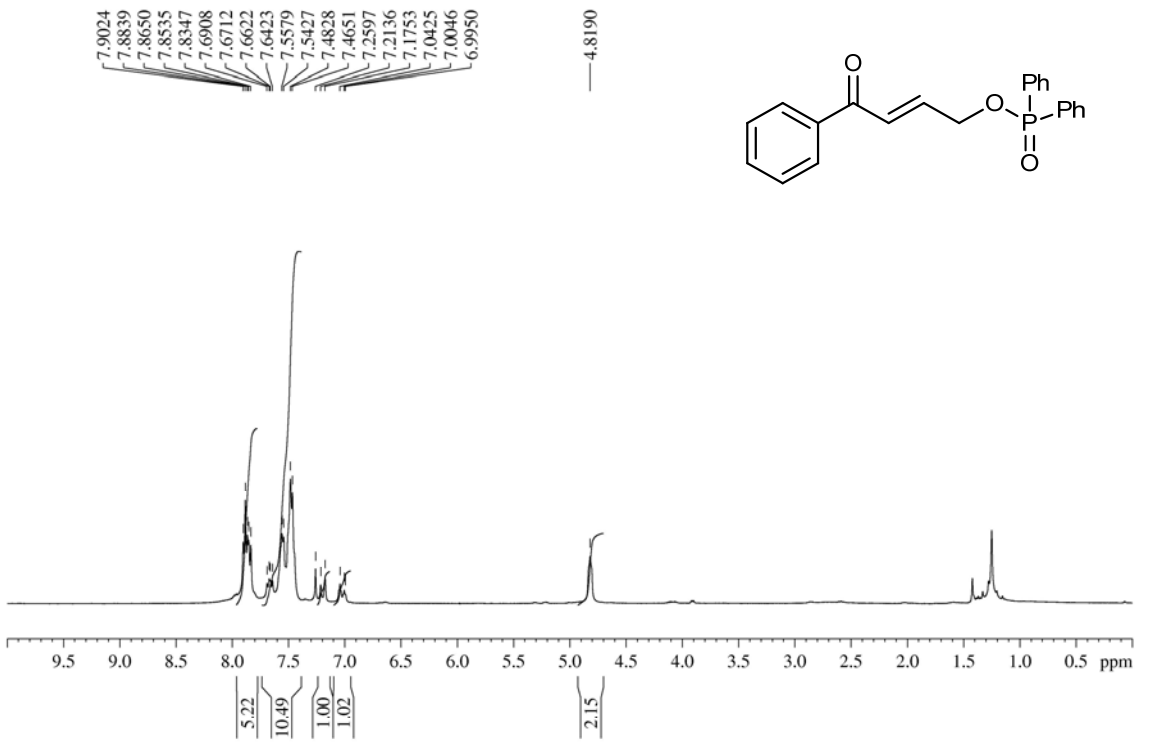
128.79
128.76
128.58
128.45
128.16
111.65
111.59
77.32
77.00
76.68
63.94
63.88
36.91
36.85
36.64
24.49
NC
CN
O
Ph
O
P
Ph
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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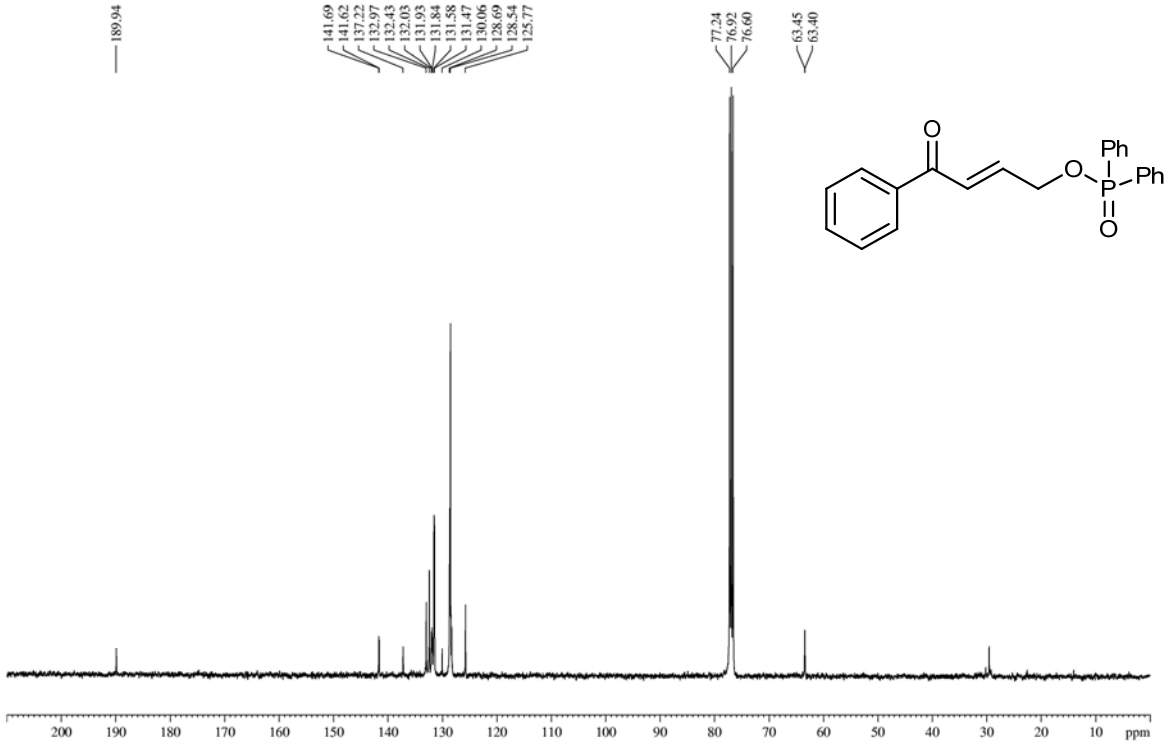
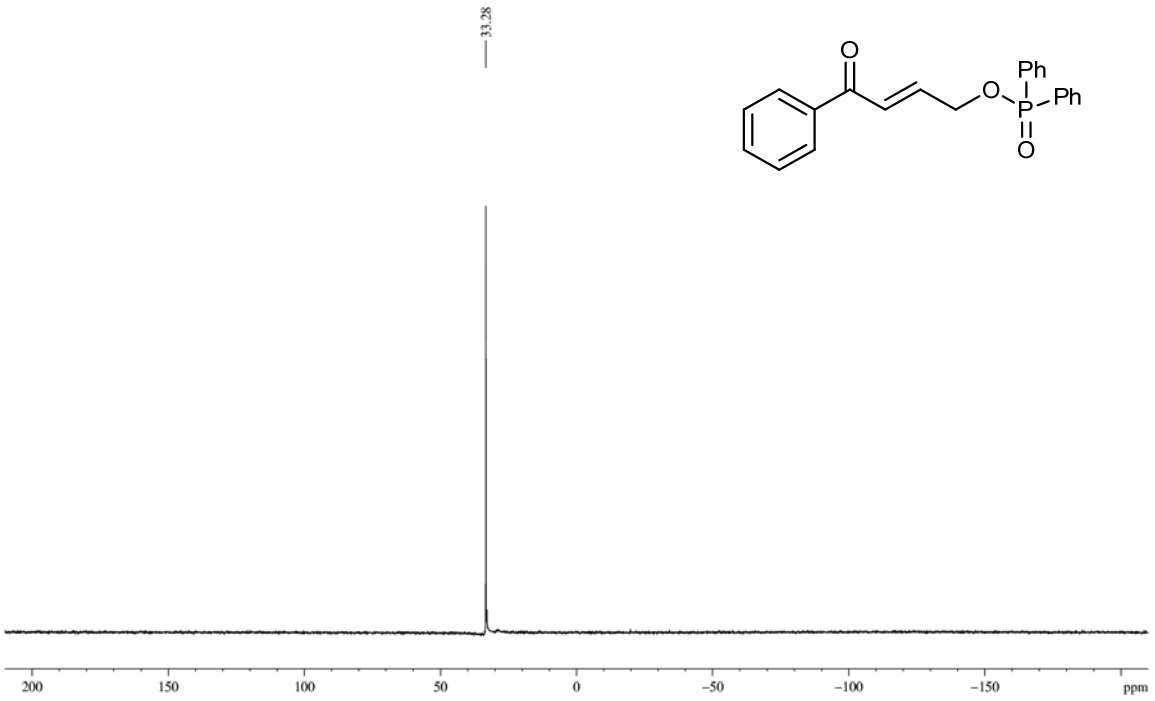
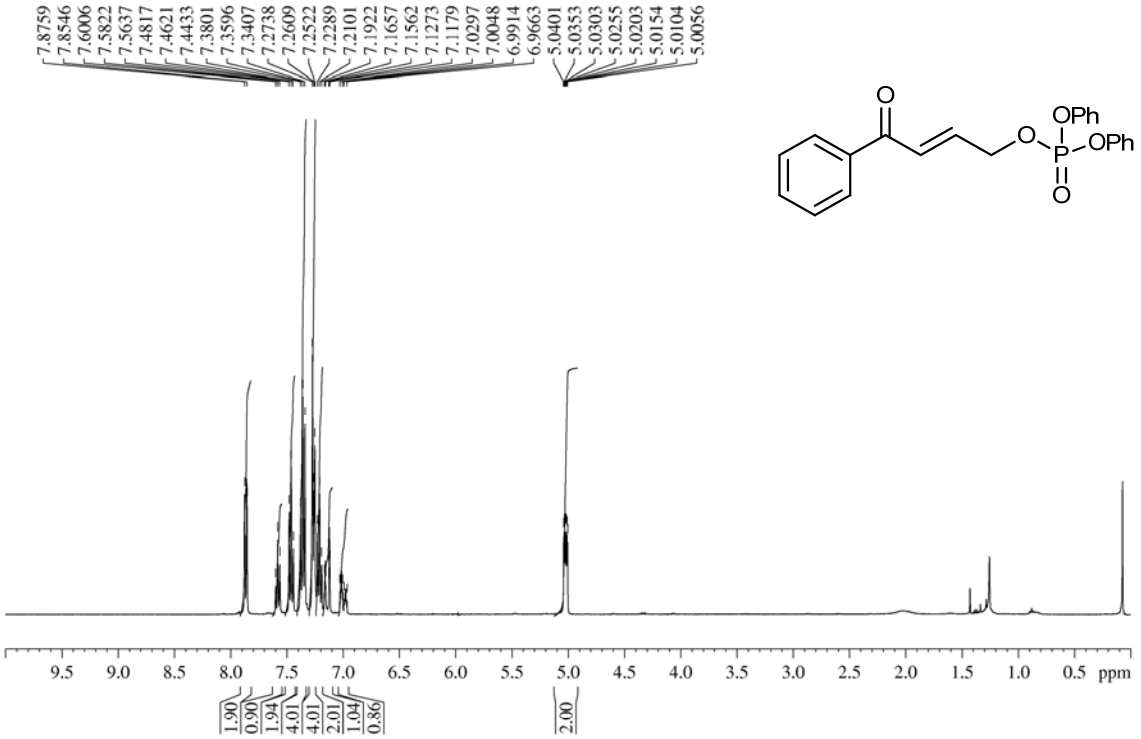
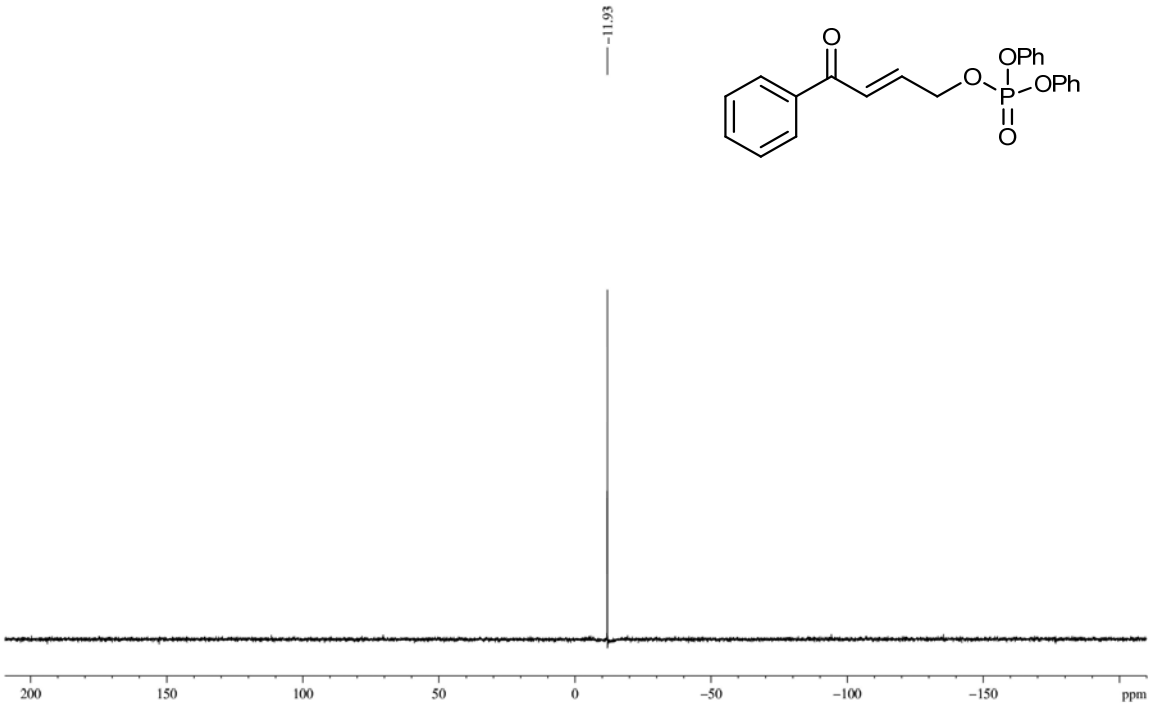
7.6712
7.6622
7.6423
7.5579
7.5427
7.4828
7.4651
7.2597
7.2136
7.1753
7.0425
7.0046
6.9950
4.8190
O
Ph
O
P
Ph
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.22
10.49
1.00
1.02
2.15


189.94
141.69
141.62
137.22
132.97
132.43
132.03
131.93
131.84
131.58
131.47
130.06
128.69
128.54
125.77
77.24
76.92
76.60
63.45
63.40
O
Ph
O
P
Ph
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



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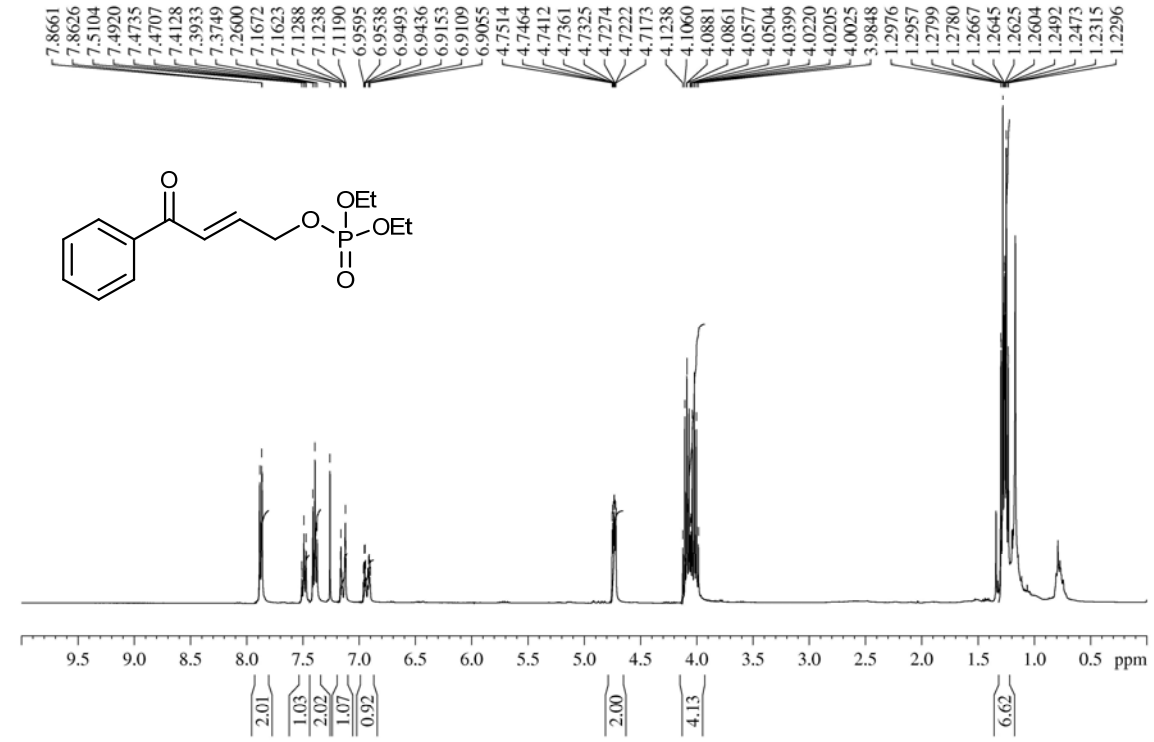
O
OPh
O
P
OPh
O
200
150
100
50
0
−50
−100
−150
ppm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7.3749
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7.1672
7.1623
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7.1238
7.1190
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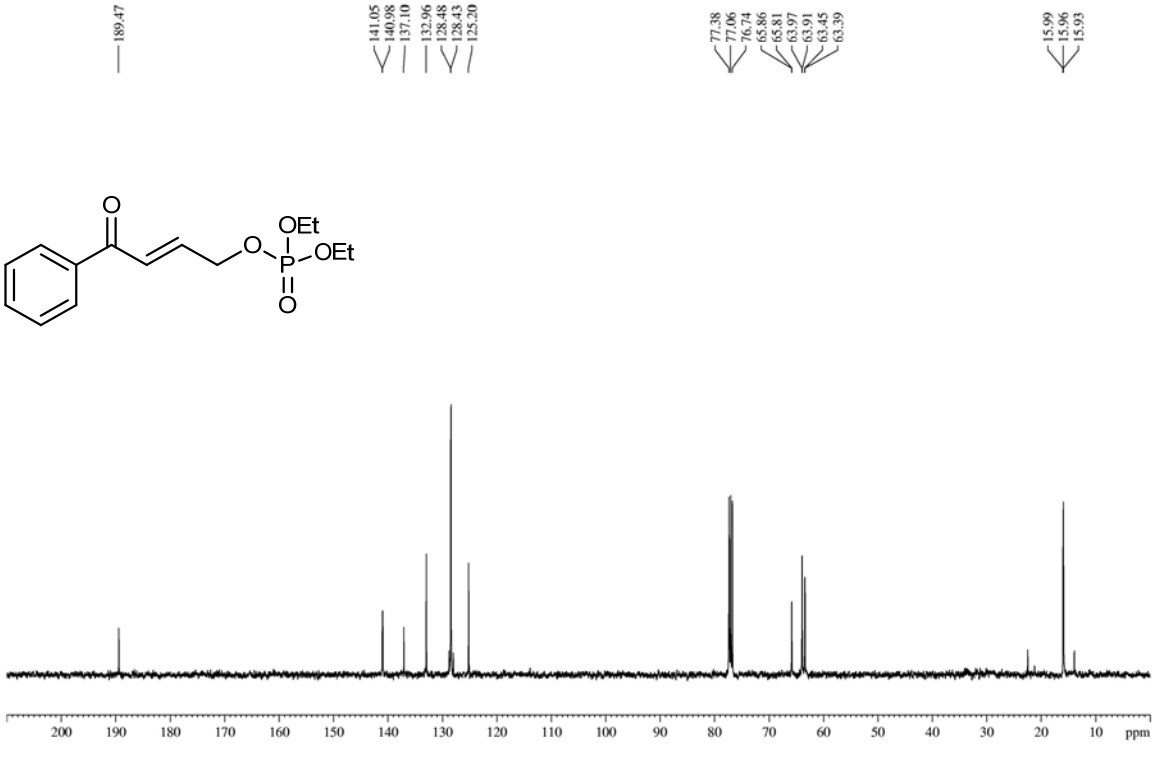
6.9538
6.9493
6.9436
6.9153
6.9109
6.9055
4.7514
4.7464
4.7412
4.7361
4.7325
4.7274
4.7222
4.7173
4.1238
4.1060
4.0881
4.0861
4.0577
4.0504
4.0399
4.0220
4.0205
4.0025
3.9848
1.2976
1.2957
1.2799
1.2780
1.2667
1.2645
1.2625
1.2604
1.2492
1.2473
1.2315
1.2296
O
OEt
O
P
OEt
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01
1.03
2.02
1.07
0.92
2.00
4.13
6.62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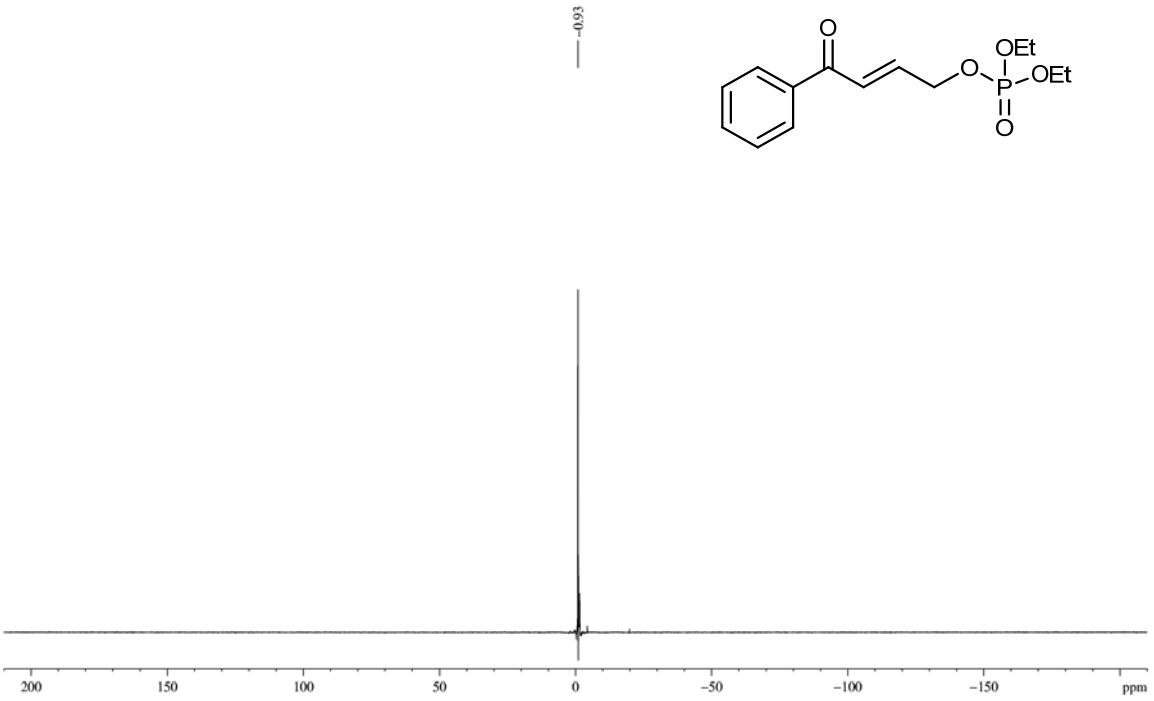
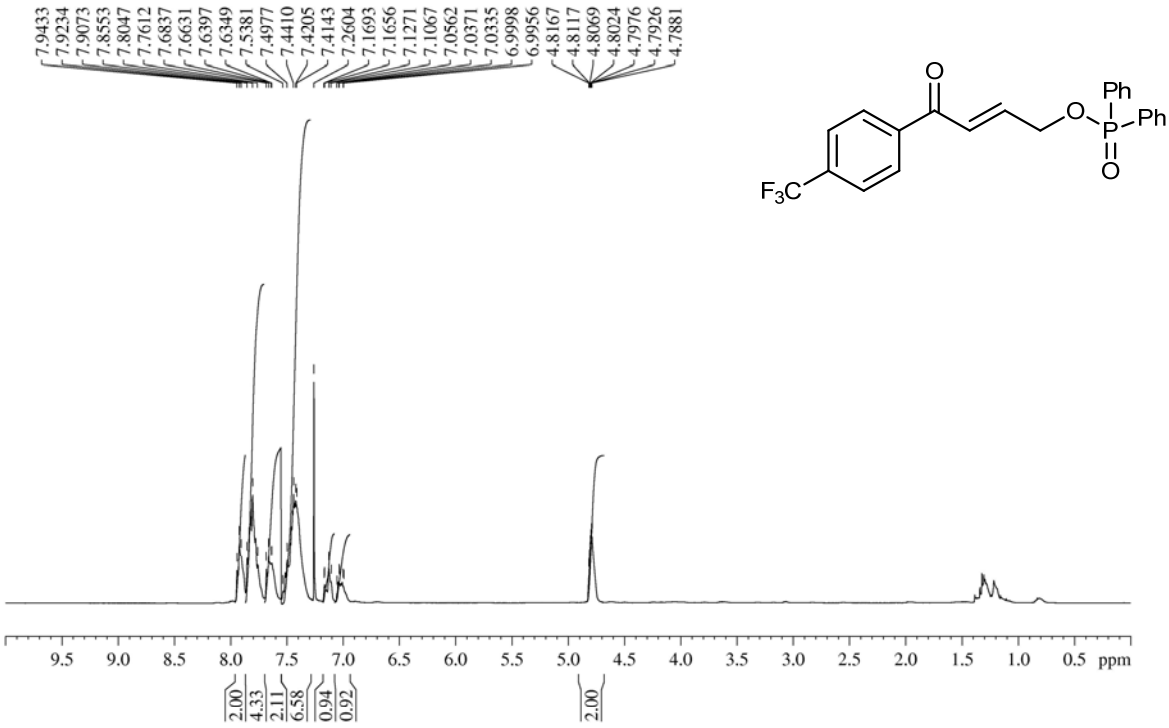
141.05
140.98
137.10
132.96
128.48
128.43
125.20
77.38
77.06
76.74
65.86
65.81
63.97
63.91
63.45
63.39
15.99
15.96
15.93
O
OEt
O
P
OEt
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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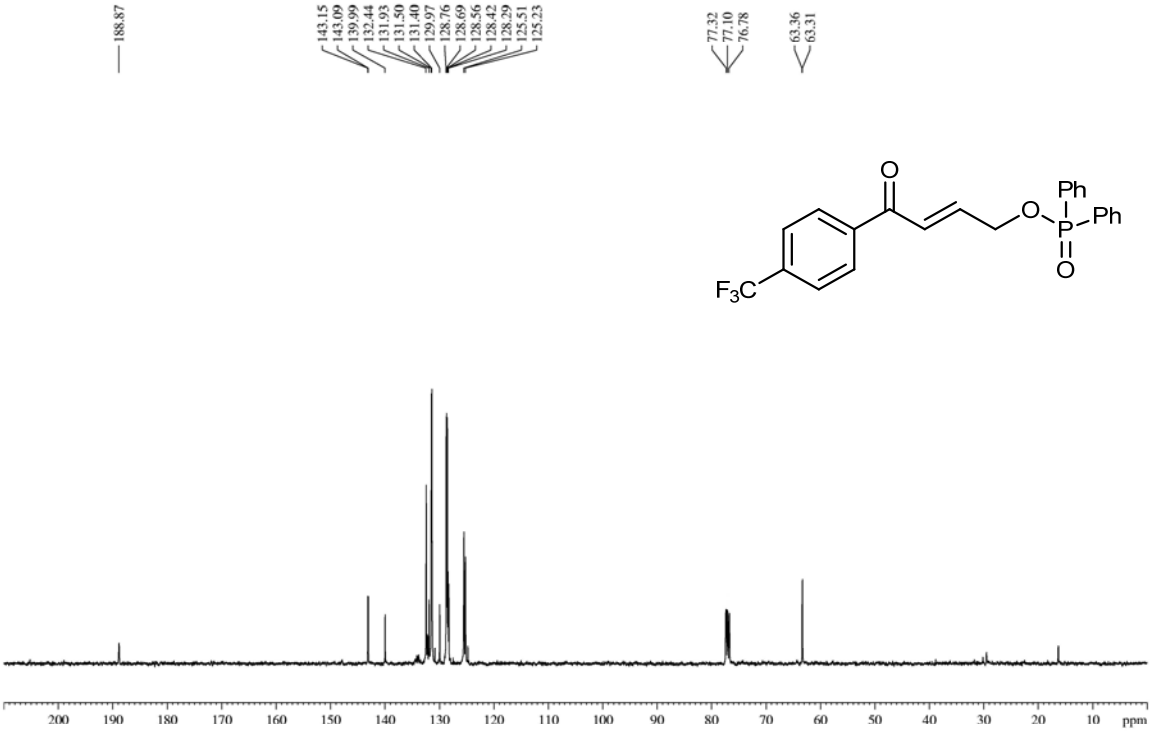
7.8553
7.8047
7.7612
7.6837
7.6631
7.6397
7.6349
7.5381
7.4977
7.4410
7.4205
7.4143
7.2604
7.1693
7.1656
7.1271
7.1067
7.0562
7.0371
7.0335
6.9998
6.9956
4.8167
4.8117
4.8069
4.8024
4.7976
4.7926
4.7881
O
Ph
O
P
Ph
O
F3C
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
4.33
2.11
6.58
0.94
0.92
2.00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139.99
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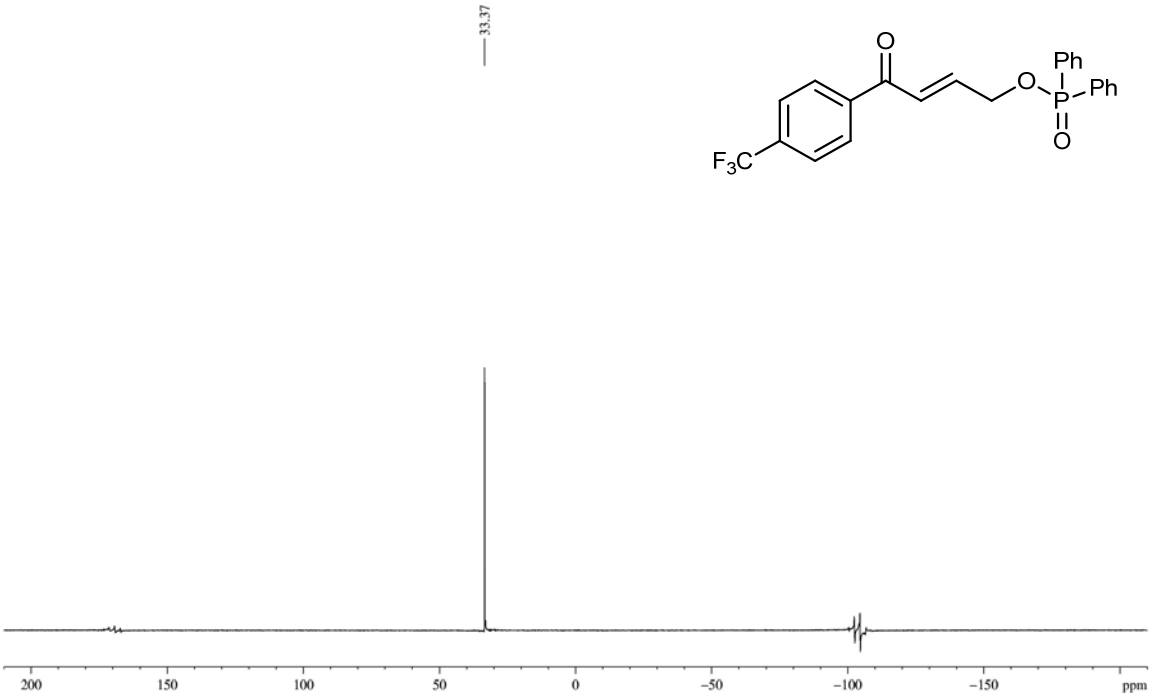
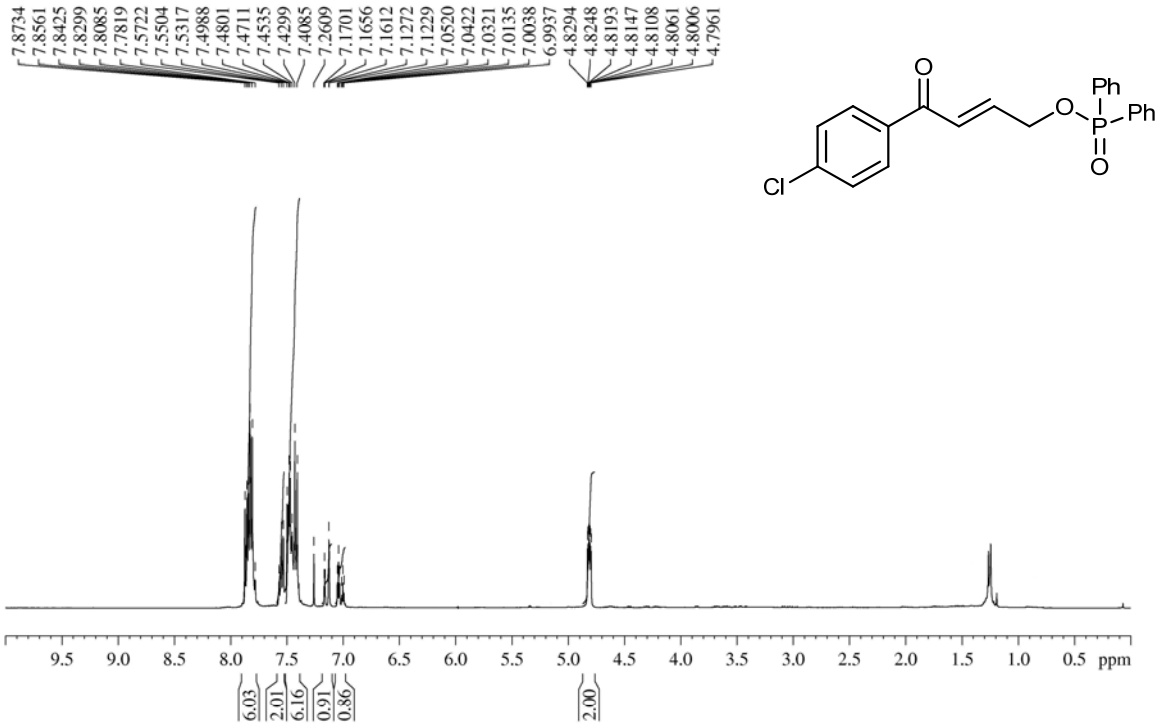
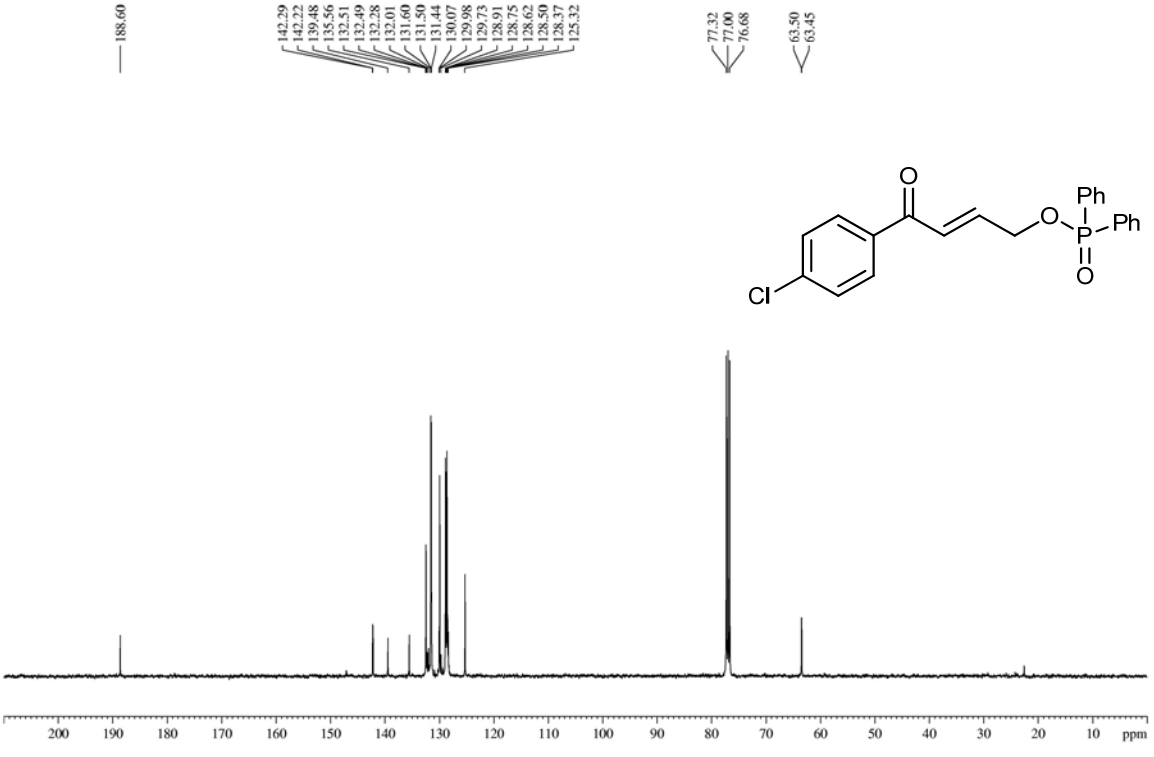
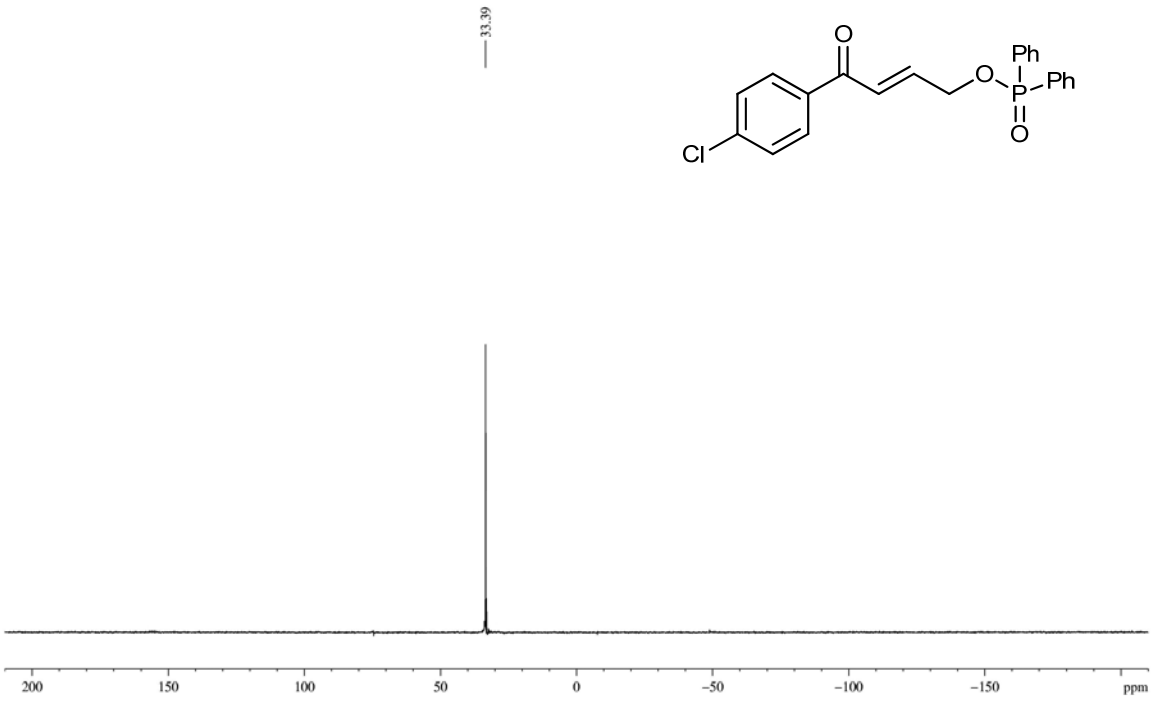
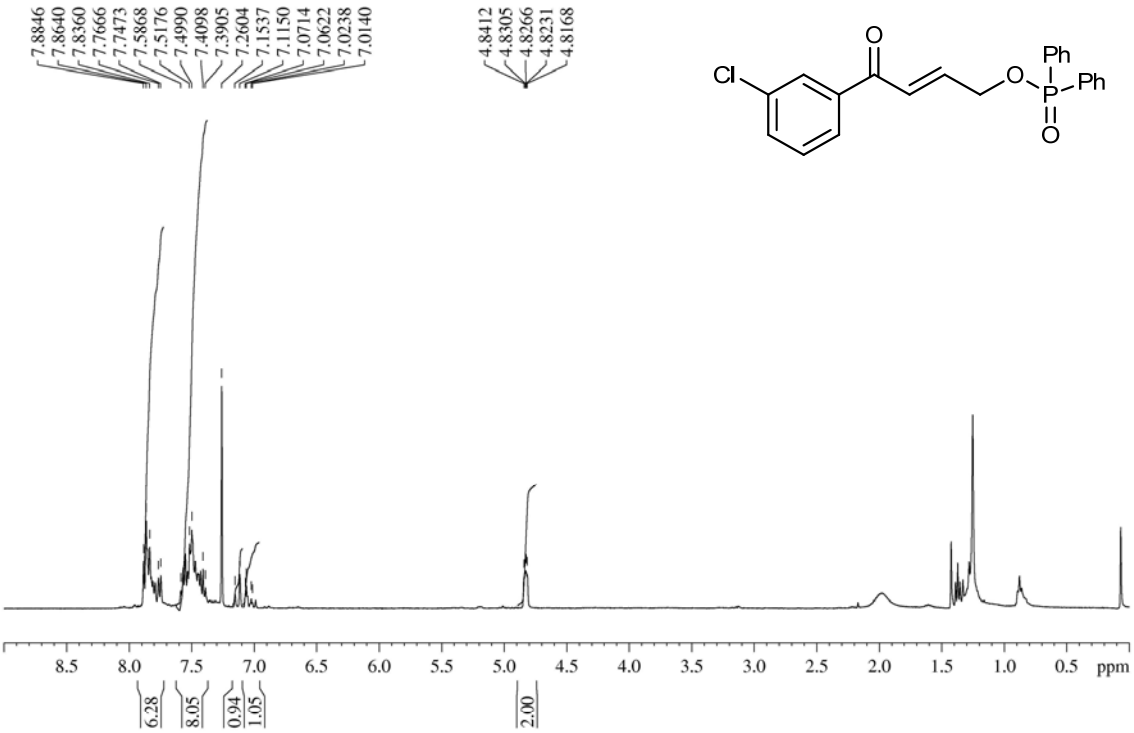
131.93
131.50
131.40
129.97
128.76
128.69
128.56
128.42
128.29
125.51
125.23
77.32
77.10
76.78
63.36
63.31
O
Ph
O
P
Ph
O
F3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

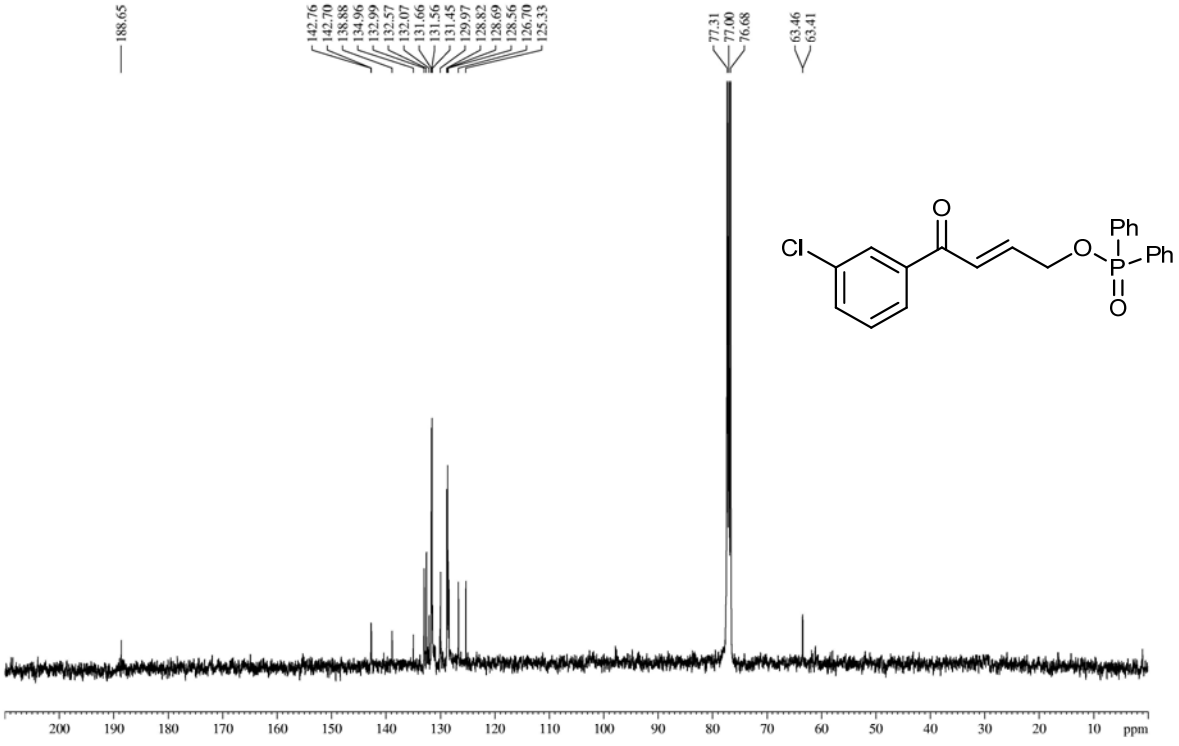


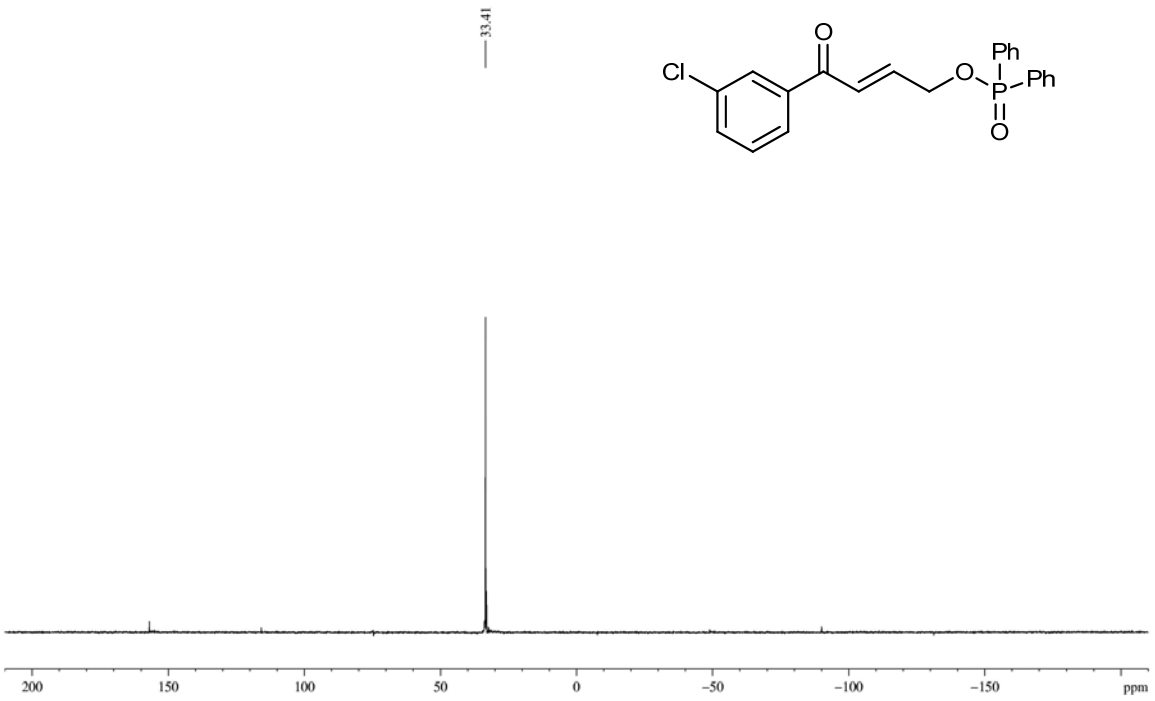


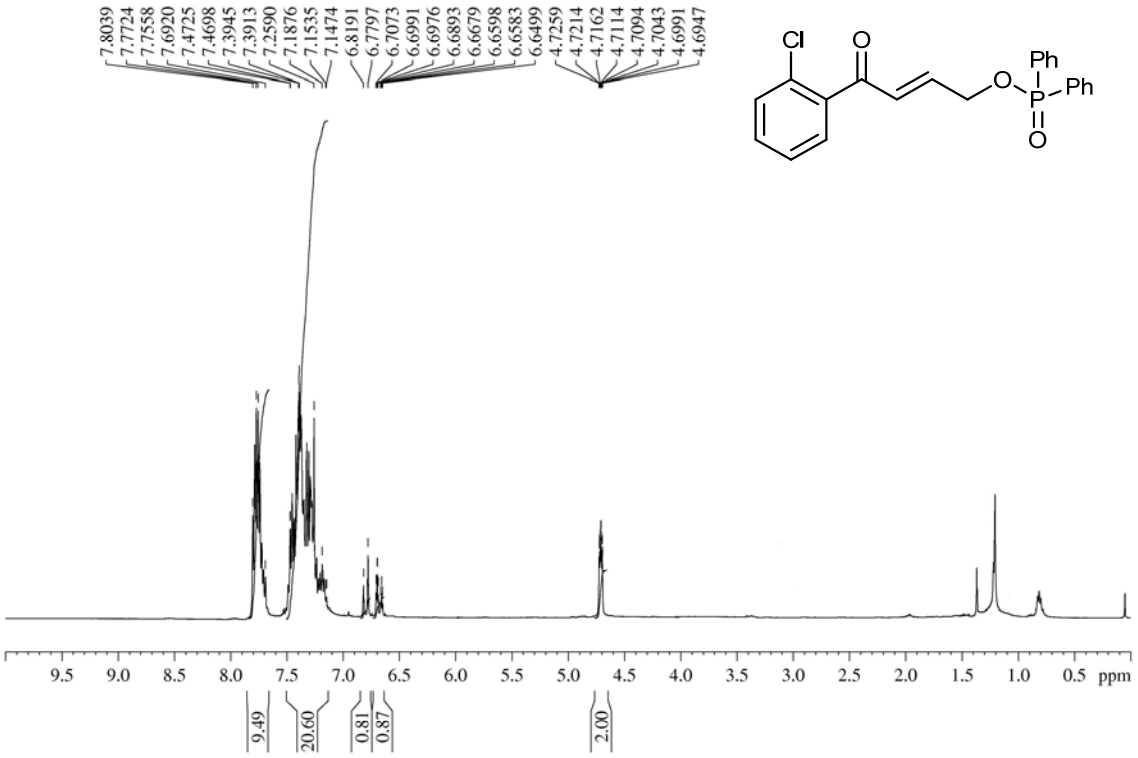


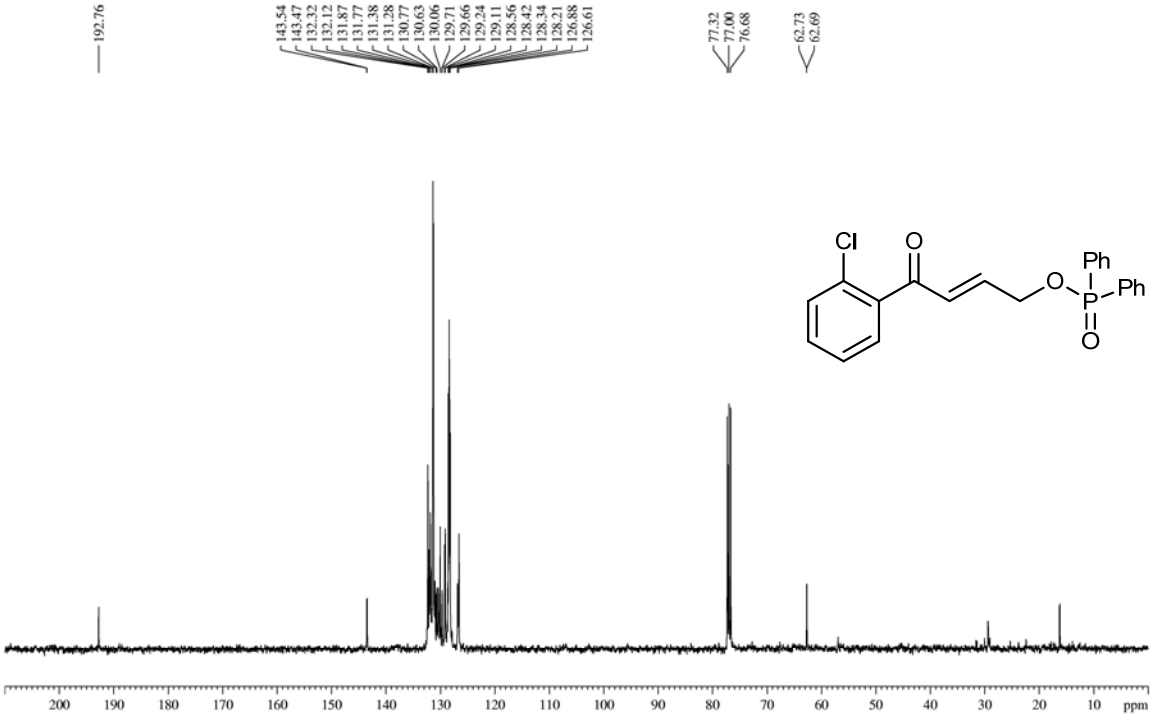


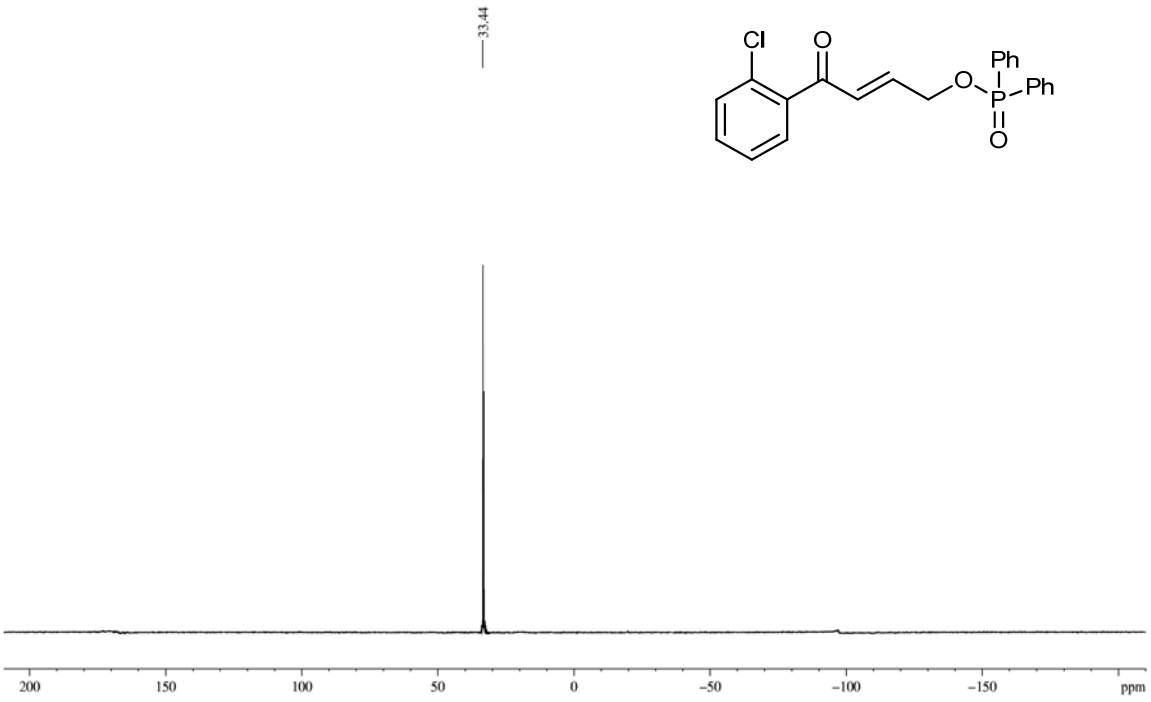


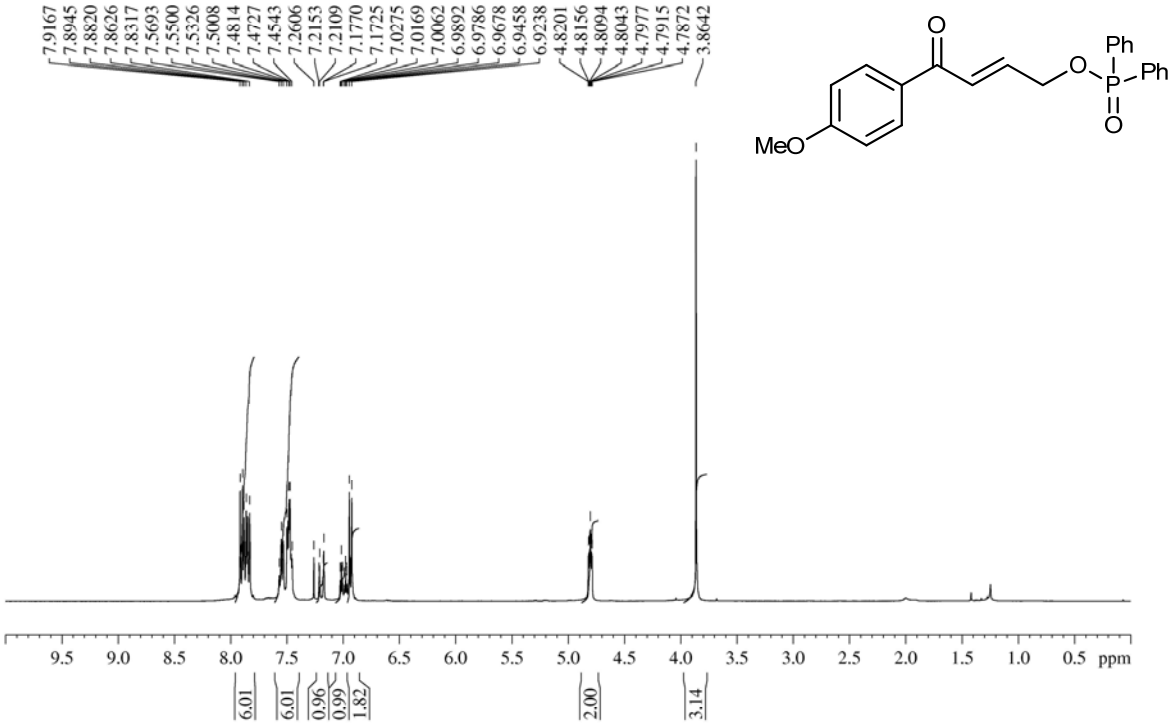


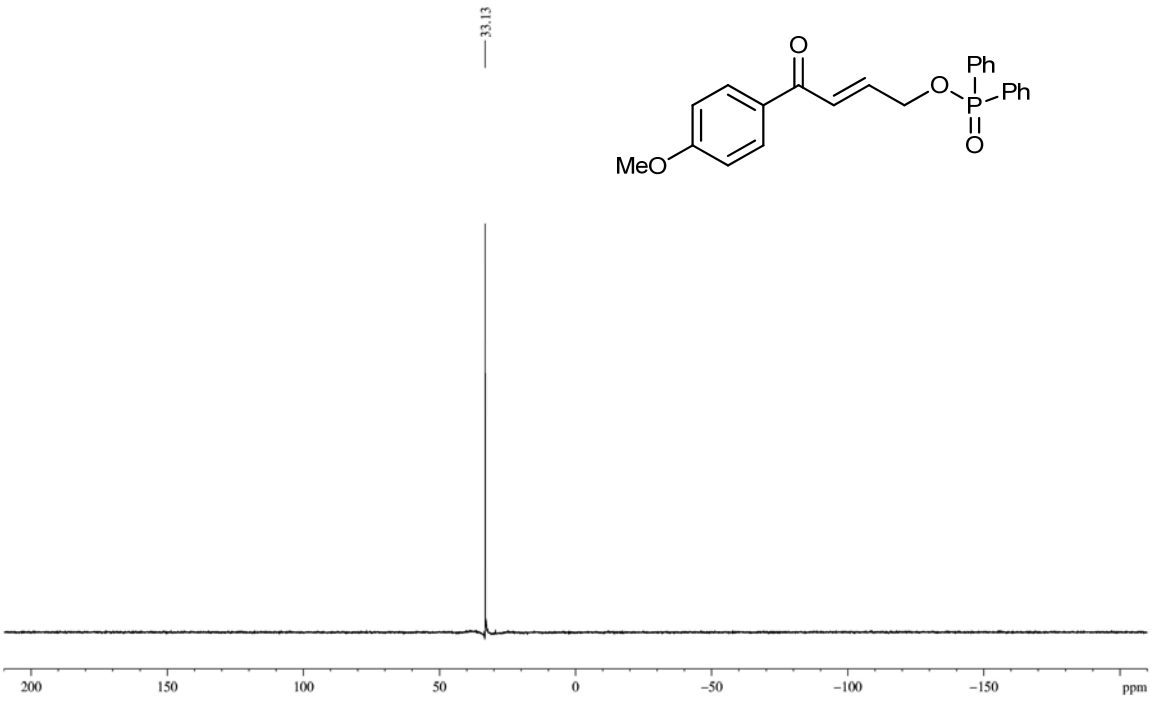


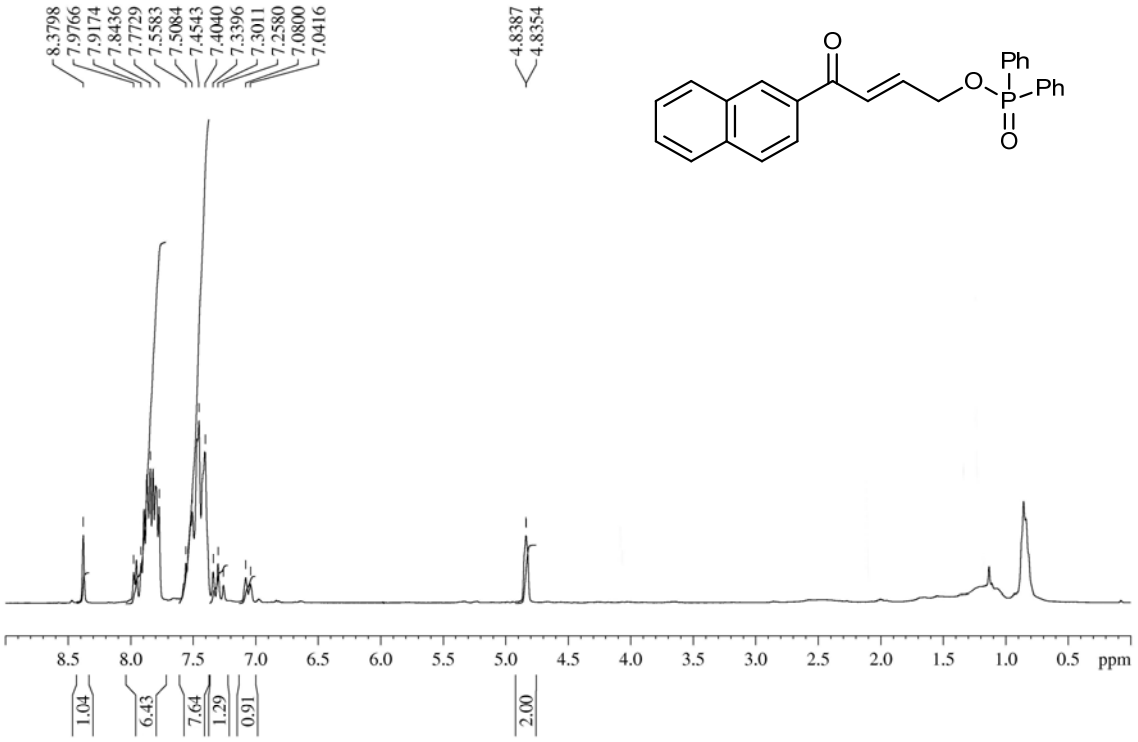


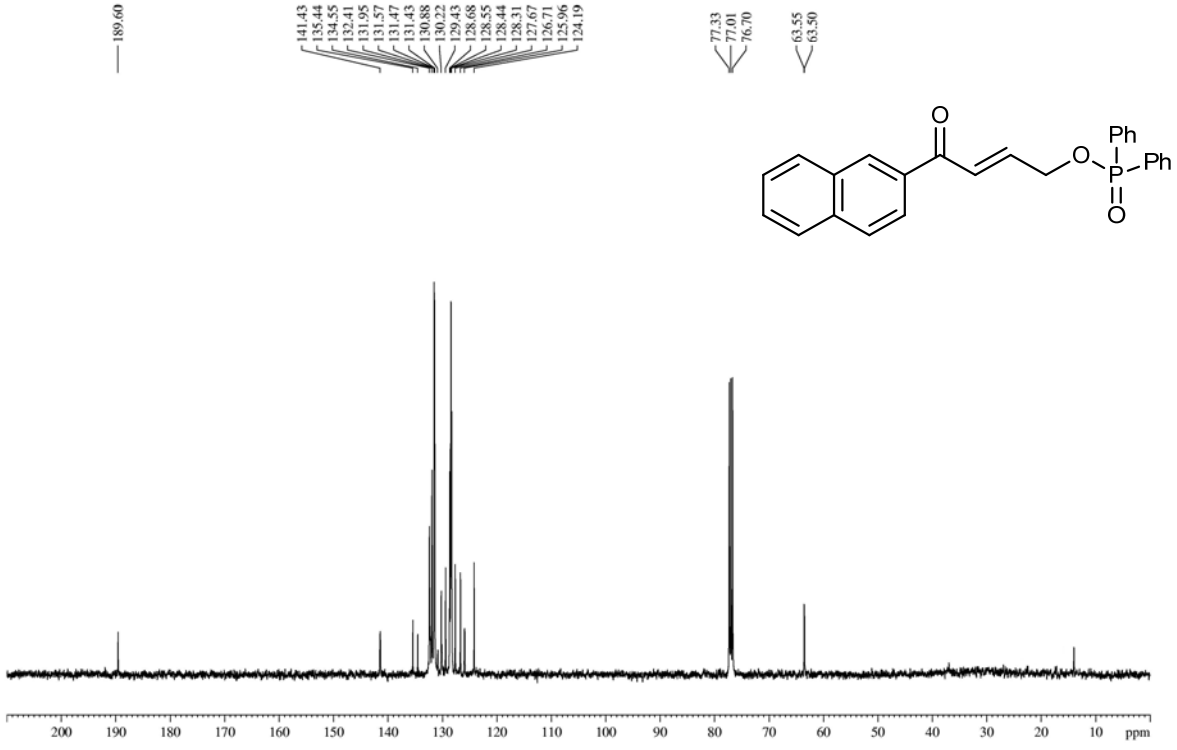


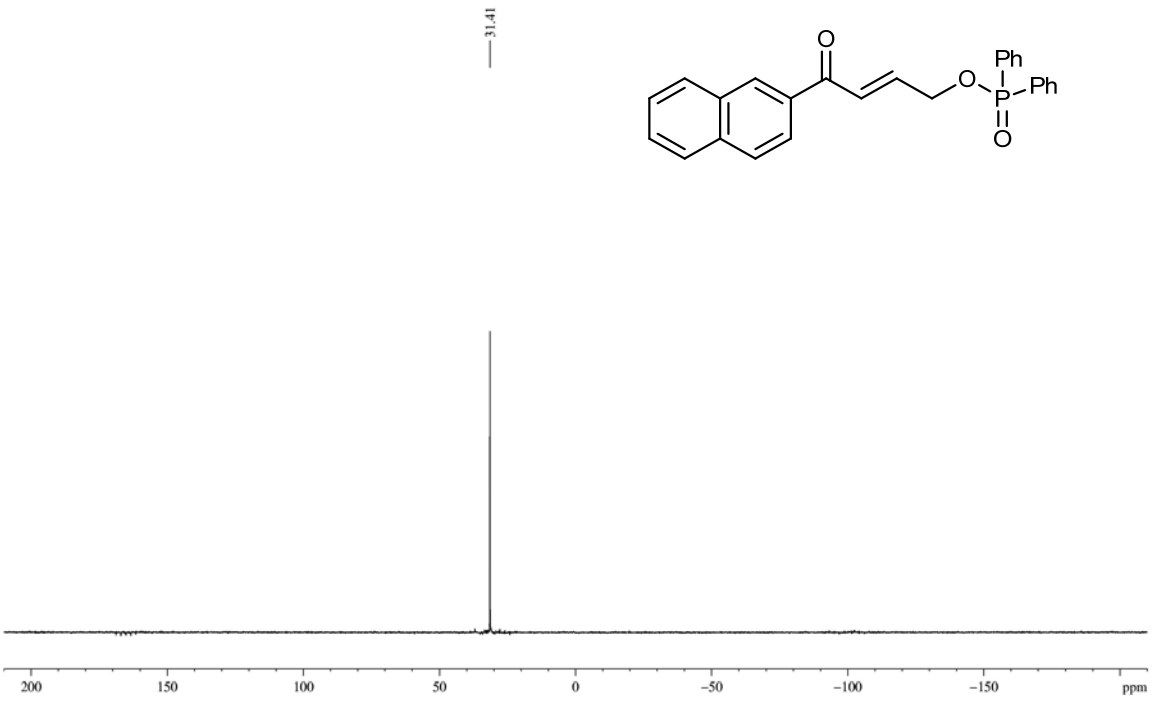




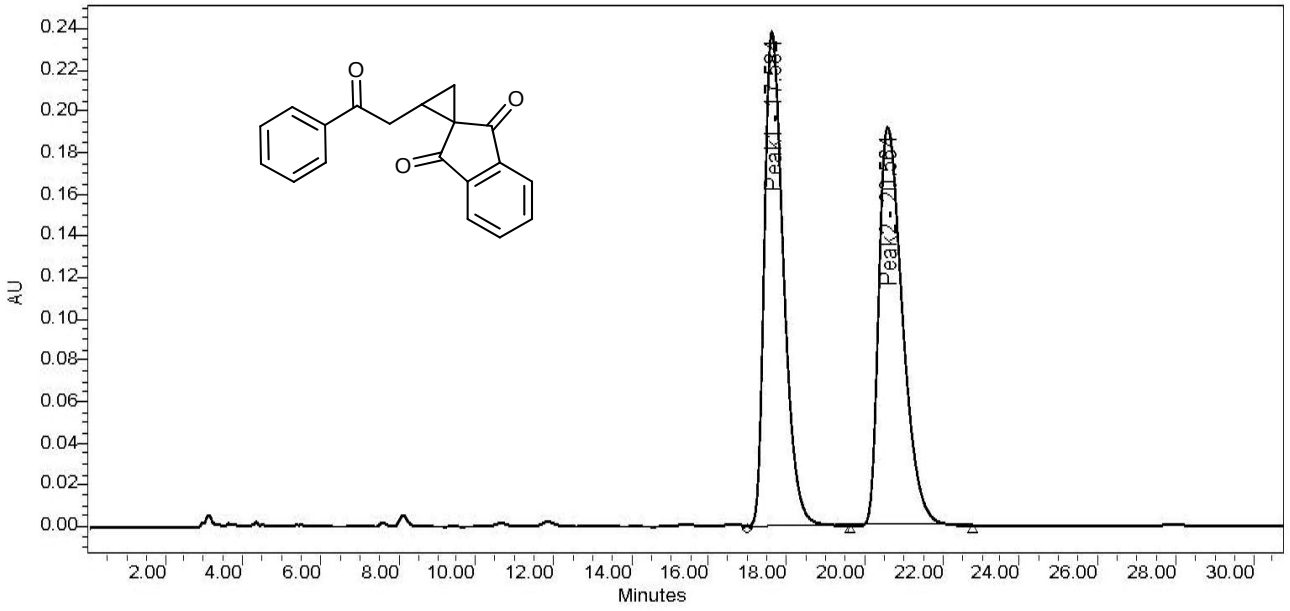




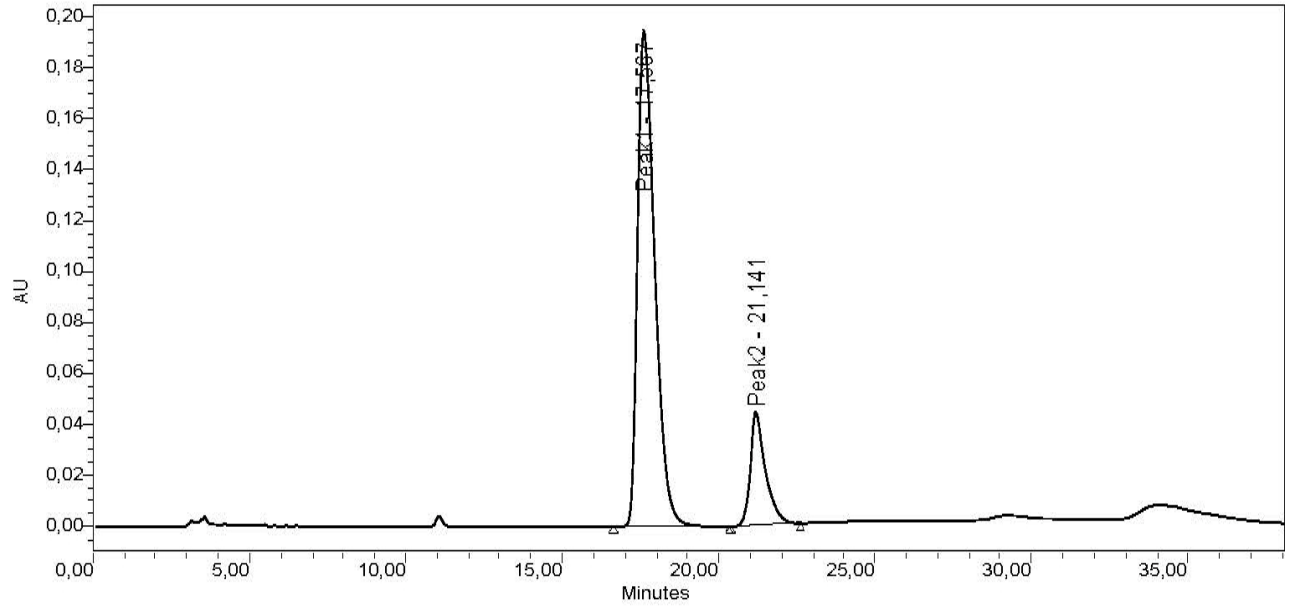




HPLC chromatograms of cyclopropane 3b



	Peak Name	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	Peak1	17.584	8171967	49.95	238284	55.38
2	Peak2	20.564	8187355	50.05	191966	44.62



	Peak Name	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	Peak1	17,567	7474028	83,31	194691	81,37
2	Peak2	21,141	1497659	16,69	44577	18,63