Supplementary Information
for Ligand-Controlled *E*/*Z* Selectivity and Enantioselectivity in Pd-Catalyzed Allylation of Benzofuranones with 1,2-Disubstituted Allylic Carbonates

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General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. ^{19}F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer. Chemical shifts are reported in ppm from benzotrifluoride (−64.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were measured on a Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, 40-50 μm; FUJI SILYSIA CHEMICAL Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [φ 4.6 mm x 250 mm, DAICEL CHIRALPAK AZ-3 (AZ3), CHIRALPAK AD-3 (AD3), CHIRALCEL OZ-3 (OZ3), and CHIRALPAK AY-3 (AY3), CHIRALPAK AS-H (ASH)] with hexane (H), isopropyl alcohol (IPA) and ethanol (EtOH) as eluent.

All air- and moisture-sensitive reactions were performed under an atmosphere of argon (Ar) in dried glassware. The manipulations for Pd-catalyzed reactions were carried out with standard Schlenk techniques under Ar. Toluene was supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by both A2 alumina and Q5 reactant using a GlassContour solvent dispensing system. Mesitylene was distilled from sodium metal. Benzofuranones were synthesized by following the literature methods.[1] All allylic carbonates were synthesized from the corresponding allylic alcohols.[2] Other simple chemicals were purchased and used as such.

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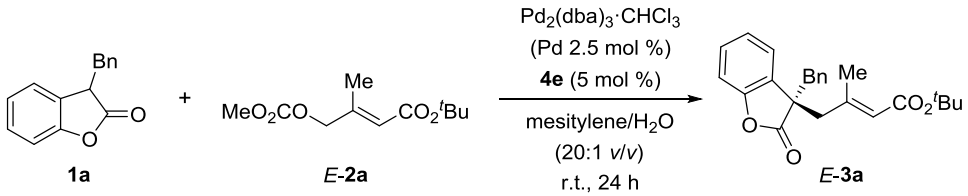
[1] (a) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. *J. Am. Chem. Soc.* **2006**, *128*, 925. (b) Azzena, U.; Pisano, L.; Pittalis, M. *Appl. Organomet. Chem*. **2008**, *22*, 523. (c) Kalinin, A. V.; Miah, M. A. J.; Chattopadhyay, S.; Tsukazaki, M.; Wicki, M.; Nguen, T.; Coelho, A. L.; Kerr, M.; Snieckus, V. *Synlett.* **1997**, 839.

[2] Matsubara, R.; Jamison, T. F. *J. Am. Chem. Soc.* **2010**, *132*, 6880.

Representative Procedure for Asymmetric Allylation of Benzofuranones with 1,2-Disubstituted Allylic Carbonates:

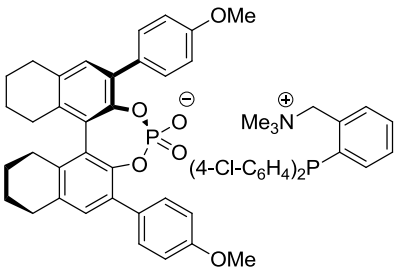


To a Schlenk flask were added $Pd_2(dba)_3{\cdot}CHCl_3$ (2.58 mg, 0.0025 mmol) and ligand **4e** (10.7 mg, 0.01 mmol), and the flask was degassed by alternating vacuum evacuation/Ar backfill. Then, mesitylene (2 mL) was added, and the resulting catalyst mixture was evacuated and refilled with Ar three times. After addition of H_2O (0.1 mL), 3-benzylbenzofuranone **1a** (44.9 mg, 0.2 mmol) and allylic carbonate *E*-**2a** (46.1 mg, 0.2 mmol) were successively introduced at room temperature. After stirring for 24 h at the same temperature, the reaction mixture was filtered through a short pad of silica gel with the aid of $CHCl_3$. The resulting filtrates were evaporated and the residue was purified by column chromatography on silica gel (H/EtOAc = 15:1 as eluent) to afford **3a** (73.4 mg, 0.194 mmol, 97% yield) as a white solid.

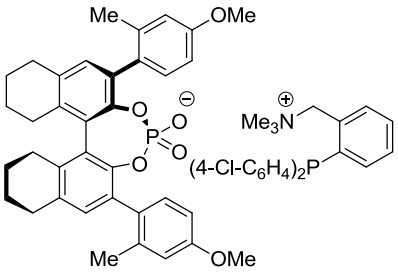
3a: $[\alpha]_D^{23}$ = –22.5 (*c* = 0.97, $CHCl_3$) for 94% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (1H, ddd, *J* = 8.2, 6.4, 2.8 Hz), 7.17-7.07 (5H, m), 6.88 (1H, d, *J* = 7.8 Hz), 6.85 (1H, d, *J* = 7.8 Hz), 6.85 (1H, d, *J* = 7.8 Hz), 5.52 (1H, s), 3.23 (1H, d, *J* = 13.3 Hz), 3.12 (1H, d, *J* = 13.3 Hz), 2.99 (1H, d, *J* = 13.5 Hz), 2.75 (1H, d, *J* = 13.5 Hz), 1.75 (3H, s), 1.40 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 165.6, 153.0, 151.2, 134.4, 130.2, 129.2, 128.2, 128.1, 127.3, 124.8, 123.9, 122.4, 111.0, 80.0, 54.1, 48.3, 45.4, 28.3, 19.6; IR (neat) 2978, 2936, 2926, 1798, 1788, 1711, 1462, 1153, 1070, 881, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{26}O_4Na_1^+$ ($[M+Na]^+$) 401.1723. Found 401.1722.; HPLC AZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 13.5 min (minor), 14.2 min (major).

Characterization data for the other products **3** were described below

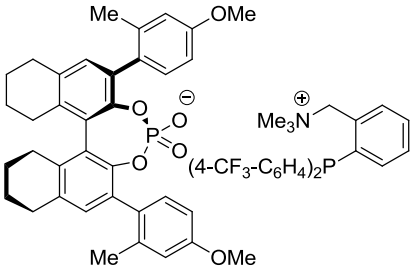
Characterization Data for Ion-Paired Chiral Ligand :



4c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (4H, d, *J* = 8.7 Hz), 7.68-7.63 (1H, m), 7.43-7.38 (2H, m), 7.33 (2H, d, *J* = 9.1 Hz), 7.33 (2H, d, *J* = 9.1 Hz), 7.09-7.02 (7H, m), 6.83 (4H, d, *J* = 8.7 Hz), 4.77 (1H, d, *J* = 13.5 Hz), 4.72 (1H, d, *J* = 13.5 Hz), 3.74 (6H, s), 2.93 (9H, s), 2.90-2.80 (2H, m), 2.80-2.70 (2H, m), 2.70-2.60 (2H, m), 2.31-2.22 (2H, m), 1.81-1.72 (6H, m), 1.63-1.49 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 146.0 (d, $J_{P\text{-}C}$ = 9.7 Hz), 138.2 (d, $J_{P\text{-}C}$ = 15.5 Hz), 136.1, 136.1 (d, $J_{P\text{-}C}$ = 24.5 Hz), 135.7 (d, $J_{P\text{-}C}$ = 3.9 Hz), 135.5, 134.8 (d, $J_{P\text{-}C}$ = 21.3 Hz), 134.7 (d, $J_{P\text{-}C}$ = 20.3 Hz), 133.5 (d, $J_{P\text{-}C}$ = 3.9 Hz), 133.4 (d, $J_{P\text{-}C}$ = 3.9 Hz), 133.2, 132.9, 132.7, 131.9, 131.1, 130.9, 130.7, 130.7 (d, $J_{P\text{-}C}$ = 9.7 Hz), 130.1, 129.5 (d, $J_{P\text{-}C}$ = 7.7 Hz), 129.1, 113.2, 65.5 (d, $J_{P\text{-}C}$ = 21.3 Hz), 55.4, 52.7, 29.4, 27.9, 23.1, 23.0, one peak for aromatic carbon was not found probably due to overlapping; ^{31}P NMR (162 MHz, $CDCl_3$) δ 1.7, –16.9; IR (neat) 2926, 2855, 2835, 1477, 1387, 1063, 1013, 833, 810 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{22}H_{23}Cl_2N_1P_1^+$ ($[M–X]^+$) 402.0940. Found 402.0938. (ESI, negative ion mode) Calcd for $C_{34}H_{32}O_6P_1^-$ ($[X]^-$) 567.1942. Found 567.1931.; $[\alpha]_D^{19}$ = –171.8 (*c* = 0.97, $CHCl_3$)

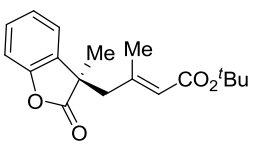


4d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.61 (1H, m), 7.49-7.38 (4H, m), 7.34 (2H, d, J = 8.2 Hz), 7.33 (2H, d, J = 8.2 Hz), 7.15-7.03 (5H, m), 6.86 (2H, s), 6.66 (2H, s), 6.66-6.61 (2H, m), 4.73 (1H, d, J = 13.1 Hz), 4.67 (1H, d, J = 13.1 Hz), 3.72 (6H, s), 2.85 (9H, s), 2.85-2.66 (6H, m), 2.38-2.26 (2H, m), 2.18 (6H, s), 1.84-1.73 (6H, m), 1.62-1.53 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 146.4 (d, $J_{P\text{-}C}$ = 8.7 Hz), 138.7, 138.3 (d, $J_{P\text{-}C}$ = 16.4 Hz), 136.1, 136.1, 135.8 (d, $J_{P\text{-}C}$ = 3.9 Hz), 135.6, 134.8 (d, $J_{P\text{-}C}$ = 20.3 Hz), 134.7 (d, $J_{P\text{-}C}$ = 20.3 Hz), 133.5 (d, $J_{P\text{-}C}$ = 6.8 Hz), 133.4 (d, $J_{P\text{-}C}$ = 6.8 Hz), 133.4, 133.3, 133.2, 133.1, 132.4, 132.4 (d, $J_{P\text{-}C}$ = 17.4 Hz), 131.1, 130.9, 130.7, 129.5 (d, $J_{P\text{-}C}$ = 6.8 Hz), 128.7, 114.7, 110.1, 65.6 (d, $J_{P\text{-}C}$ = 20.3 Hz), 55.3, 52.8, 29.4, 27.9, 23.2, 23.1, 20.8, one peak for aromatic carbon was not found probably due to overlapping; ^{31}P NMR (162 MHz, $CDCl_3$) δ 2.2, –17.0; IR (neat) 2931, 2857, 2835, 1607, 1271, 1045, 818, 731 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{22}H_{23}Cl_2N_1P_1^+$ ([M–X]$^+$) 402.0940. Found 402.0940. (ESI, negative ion mode) Calcd for $C_{36}H_{36}O_6P_1^-$ ([X]$^-$) 595.2255. Found 595.2245.; $[\alpha]_D^{19}$ = –69.8 (c = 0.99, $CHCl_3$).

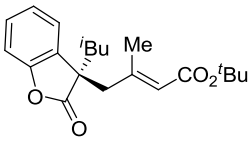


4e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.71 (1H, m), 7.63 (2H, d, J = 7.8 Hz), 7.62 (2H, d, J = 7.8 Hz), 7.53-7.41 (2H, m), 7.40-7.31 (2H, m), 7.31-7.24 (4H, m), 7.13-7.08 (1H, m), 6.85 (2H, s), 6.44 (2H, s), 6.44-6.61 (2H, m), 4.85 (1H, d, J = 13.1 Hz), 4.77 (1H, d, J = 13.1 Hz), 3.72 (6H, s), 2.89 (9H, s), 2.86-2.66 (6H, m), 2.35-2.26 (2H, m), 2.16 (6H, s), 1.84-1.71 (6H, m), 1.65-1.55 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 146.3 (d, $J_{P\text{-}C}$ = 8.7 Hz), 139.7 (d, $J_{P\text{-}C}$ = 9.7 Hz), 139.6 (d, $J_{P\text{-}C}$ = 9.7 Hz), 138.6, 137.1 (d, $J_{P\text{-}C}$ = 14.5 Hz), 136.0 (d, $J_{P\text{-}C}$ = 20.3 Hz), 136.0 (d, $J_{P\text{-}C}$ = 4.8 Hz), 133.7 (d, $J_{P\text{-}C}$ = 20.3 Hz), 133.6 (d, $J_{P\text{-}C}$ = 19.4 Hz), 133.6, 132.4, 132.3 (d, $J_{P\text{-}C}$ = 20.3 Hz), 131.7 (q, $J_{F\text{-}C}$ = 33.9 Hz), 131.7 (q, $J_{F\text{-}C}$ = 33.9 Hz), 131.1, 130.9 (d, $J_{P\text{-}C}$ = 2.9 Hz), 128.6, 125.9 (q, $J_{F\text{-}C}$ = 3.9 Hz), 125.9 (q, $J_{F\text{-}C}$ = 3.9 Hz), 123.8 (q, $J_{F\text{-}C}$ = 276.9 Hz), 123.8 (q, $J_{F\text{-}C}$ = 276.9 Hz), 114.8, 110.1, 65.5 (d, $J_{P\text{-}C}$ = 21.3 Hz), 55.2, 52.7, 29.3, 27.9, 23.1, 23.0, 20.7, four peaks for aromatic carbons were not found probably due to overlapping; ^{31}P NMR (162 MHz, $CDCl_3$) δ 2.3, –15.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (neat) 3017, 1607, 1323, 1206, 1098, 1061, 766, 718 cm^{-1}; HRMS (ESI, positive ion mode) Calcd for $C_{24}H_{23}F_6N_1P_1^+$ ([M–X]$^+$) 470.1467. Found 470.1455. (ESI, negative ion mode) Calcd for $C_{36}H_{36}O_6P_1^-$ ([X]$^-$) 595.2255. Found 595.2245.; $[\alpha]_D^{19}$ = –80.4 (c = 0.97, $CHCl_3$).

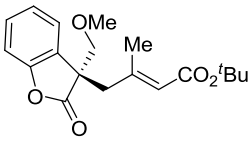
Characterization Data for the Alkylated Product 3:



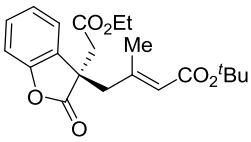
3b: The reaction was stirred for 48 h. $[\alpha]_D^{23}$ = +64.1 (c = 0.96, $CHCl_3$) for 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (1H, m), 7.22-7.14 (2H, m), 7.11 (1H, d, J = 8.2 Hz), 5.48 (1H, s), 2.82 (1H, d, J = 13.3 Hz), 2.61 (1H, d, J = 13.3 Hz), 1.77 (3H, s), 1.54 (3H, s), 1.41 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 165.6, 152.6, 151.4, 130.8, 129.1, 124.3, 123.8, 122.2, 111.1, 79.9, 49.2, 47.7, 28.2, 25.6, 19.6; IR (neat) 2976, 2932, 1790, 1721, 1694, 1464 1364, 1233, 1157, 878 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{22}O_4Na_1^+$ ([M+Na]$^+$) 325.1410. Found 325.1408.; HPLC AZ3, H/IPA = 99:1, flow rate = 0.5 mL/min, λ = 210 nm, 19.0 min (minor), 20.5 min (major).



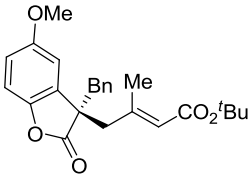
3c: The reaction was stirred for 98 h. $[\alpha]_D^{23}$ = +33.4 (*c* = 1.0, $CHCl_3$) for 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (1H, ddd, *J* = 7.8, 5.5, 3.6 Hz), 7.19-7.14 (2H, m), 7.10 (1H, d, *J* = 7.8 Hz), 5.43 (1H, d, *J* = 1.4 Hz), 2.76 (1H, d, *J* = 12.8 Hz), 2.56 (1H, d, *J* = 12.8 Hz), 1.98 (1H, dd, *J* = 14.2, 7.8 Hz), 1.86 (1H, dd, *J* = 14.2, 5.3 Hz), 1.70 (3H, d, *J* = 1.4 Hz), 1.40 (9H, s), 1.39-1.30 (1H, m), 0.74 (3H, d, *J* = 6.9 Hz), 0.66 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 165.6, 153.2, 150.9, 129.1, 124.3, 124.2, 122.4, 111.1, 79.9, 52.2, 50.7, 47.4, 28.3, 25.5, 24.1, 22.8, 19.8, one peak for aromatic carbon was not found probably due to overlapping; IR (neat) 2959, 2934, 1803, 1788, 1711, 1639, 1462, 1393, 1236, 1036, 868 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{28}O_4Na_1^+$ ($[M+Na]^+$) 367.1880. Found 367.1879.; HPLC AY3, H/IPA = 99:1, flow rate = 0.5 mL/min, λ = 210 nm, 20.5 min (minor), 26.4 min (major).



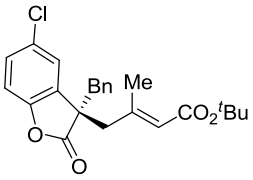
3d: The reaction was stirred for 98 h. $[\alpha]_D^{23}$ = +28.2 (*c* = 1.0, $CHCl_3$) for 88% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (1H, td, *J* = 7.8, 1.4 Hz), 7.27 (1H, td, *J* = 7.8, 1.4 Hz), 7.17 (1H, dd, *J* = 7.8, 0.9 Hz), 7.11 (1H, dd, *J* = 7.8, 0.9 Hz), 5.51 (1H, d, *J* = 1.2 Hz), 3.69 (1H, d, *J* = 12.4 Hz), 3.67 (1H, d, *J* = 12.4 Hz), 3.27 (3H, s), 2.78 (1H, d, *J* = 13.7 Hz), 2.67 (1H, d, *J* = 13.7 Hz), 1.76 (3H, d, *J* = 1.2 Hz), 1.40 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 165.5, 153.4, 150.8, 129.4, 127.9, 124.5, 124.3, 122.4, 111.0, 80.0, 77.1, 59.7, 53.3, 44.3, 28.3, 19.6; IR (neat) 3003, 2936, 1798, 1711, 1464, 1366, 1229, 1040, 881 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{24}O_5Na_1^+$ ($[M+Na]^+$) 355.1516. Found 355.1512.; HPLC OZ3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 5.7 min (minor), 6.7 min (major).



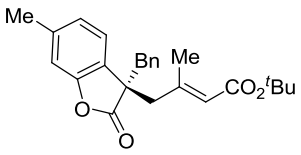
3e: The reaction was stirred for 72 h. $[\alpha]_D^{23}$ = +48.0 (*c* = 1.0, $CHCl_3$) for 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (1H, td, *J* = 7.8, 1.4 Hz), 7.20 (1H, dd, *J* = 7.8, 1.4 Hz), 7.16-7.10 (2H, m), 5.47 (1H, d, *J* = 1.4 Hz), 3.96 (1H, dq, *J* = 11.0, 7.3 Hz), 3.90 (1H, dq, *J* = 11.0, 7.3 Hz), 3.13 (1H, d, *J* = 16.7 Hz), 2.95 (1H, d, *J* = 16.7 Hz), 2.71 (1H, d, *J* = 12.8 Hz), 2.61 (1H, d, *J* = 12.8 Hz), 1.75 (3H, d, *J* = 1.4 Hz), 1.41 (9H, s), 1.02 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 168.8, 165.3, 153.7, 149.8, 129.6, 128.2, 124.1, 123.6, 123.1, 111.0, 80.0, 61.2, 49.5, 48.7, 42.3, 28.2, 20.0, 13.8; IR (neat) 2978, 2936, 1790, 1479, 1366, 1157, 1069, 881 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{26}O_6Na_1^+$ ($[M+Na]^+$) 397.1622. Found 397.1616.; HPLC OZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 20.3 min (major), 23.5 min (minor).



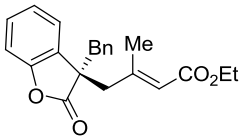
3f: The reaction was stirred for 98 h. $[\alpha]_D^{23}$ = –30.3 (*c* = 1.0, $CHCl_3$) for 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.10 (3H, m), 6.89 (2H, dd, *J* = 7.8, 1.4 Hz), 6.81 (1H, d, *J* = 8.7 Hz), 6.74 (1H, dd, *J* = 8.7, 2.8 Hz), 6.68 (1H, d, *J* = 2.8 Hz), 5.53 (1H, d, *J* = 1.2 Hz), 3.79 (3H, s), 3.20 (1H, d, *J* = 13.3 Hz), 3.10 (1H, d, *J* = 13.3 Hz), 2.98 (1H, d, *J* = 13.3 Hz), 2.73 (1H, d, *J* = 13.3 Hz), 1.78 (3H, d, *J* = 1.2 Hz), 1.40 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 165.5, 156.3, 151.3, 146.9, 134.3, 130.2, 129.0, 128.2, 127.3, 122.3, 114.1, 111.4, 110.9, 80.0, 56.0, 54.6, 48.1, 45.3, 28.3, 19.5; IR (neat) 2976, 2938, 2872, 1798, 1788, 1711, 1483, 1234, 1157, 1049, 1028, 858 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{28}O_5Na_1^+$ ($[M+Na]^+$) 431.1829. Found 431.1826.; HPLC AD3, H/IPA = 97:3, flow rate = 0.5 mL/min, λ = 210 nm, 21.4 min (minor), 24,7 min (major).



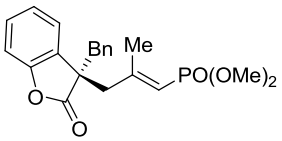
3g: The reaction was stirred for 48 h. $[\alpha]_D^{23}$ = –41.7 (*c* = 0.96, $CHCl_3$) for 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (1H, dd, *J* = 8.7, 2.3 Hz), 7.17-7.11 (4H, m), 6.86 (2H, dd, *J* = 7.6, 1.8 Hz), 6.83 (1H, d, *J* = 8.7 Hz), 5.52 (1H, d, *J* = 1.2 Hz), 3.23 (1H, d, *J* = 13.3 Hz), 3.09 (1H, d, *J* = 13.3 Hz), 3.03 (1H, d, *J* = 13.3 Hz), 2.73 (1H, d, *J* = 13.3 Hz), 1.79 (3H, d, *J* = 1.2 Hz), 1.41 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 165.4, 151.4, 150.6, 133.9, 130.1, 129.9, 129.3, 129.3, 128.3, 127.5, 124.9, 122.7, 112.1, 80.1, 54.4, 48.1, 45.3, 28.2, 19.5; IR (neat) 2976, 2932, 1813, 1805, 1796, 1711, 1470, 1366, 1236, 1227, 1032, 880, 826 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{25}O_4Cl_1Na_1^+$ ($[M+Na]^+$) 435.1334. Found 435.1331.; HPLC AD3, H/IPA = 97:3, flow rate = 0.5 mL/min, λ = 210 nm, 17.6 min (*R*), 20.6 min (*S*).



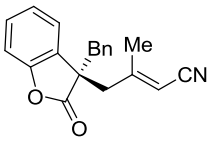
3h: The reaction was stirred for 36 h. $[\alpha]_D^{23}$ = –18.4 (*c* = 0.95, $CHCl_3$) for 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.07 (3H, m), 7.01 (1H, d, *J* = 7.8 Hz), 6.94 (1H, dd, *J* = 7.8, 0.9 Hz), 6.86 (2H, dd, *J* = 7.8, 1.4 Hz), 6.71 (1H, brs), 5.52 (1H, d, *J* = 0.9 Hz), 3.19 (1H, d, *J* = 13.3 Hz), 3.10 (1H, d, *J* = 13.3 Hz), 2.96 (1H, d, *J* = 13.3 Hz), 2.72 (1H, d, *J* = 13.3 Hz), 2.32 (3H, s), 1.75 (3H, d, *J* = 0.9 Hz), 1.40 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 165.6, 153.1, 151.6, 139.6, 134.5, 130.2, 128.1, 127.2, 124.8, 124.6, 124.5, 122.3, 111.6, 79.9, 53.9, 48.3, 45.3, 28.3, 21.8, 19.6; IR (neat) 2976, 2924, 1803, 1798, 1709, 1454, 1364, 1152, 1094, 1032, 860 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{28}O_4Na_1^+$ ($[M+Na]^+$) 415.1880. Found 415.1878.; HPLC AZ3, H/IPA = 99:1, flow rate = 0.5 mL/min, λ = 210 nm, 26.2 min (minor), 31.8 min (major).



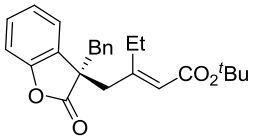
3i: The reaction was stirred for 36 h. $[\alpha]_D^{22}$ = –17.3 (*c* = 1.0, $CHCl_3$) for 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (1H, ddd, *J* = 7.8, 6.4, 2.8 Hz), 7.18-7.08 (5H, m), 6.88 (1H, d, *J* = 8.2 Hz), 6.87-6.83 (2H, m), 5.60 (1H, d, *J* = 1.4 Hz), 4.05 (2H, q, *J* = 7.3 Hz), 3.24 (1H, d, *J* = 13.3 Hz), 3.13 (1H, d, *J* = 13.3 Hz), 3.03 (1H, d, *J* = 13.3 Hz), 2.79 (1H, d, *J* = 13.3 Hz), 1.80 (3H, d, *J* = 1.4 Hz), 1.21 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 166.1, 153.1, 153.0, 134.3, 130.2, 129.3, 128.2, 127.9, 127.4, 124.8, 124.0, 120.6, 111.0, 59.8, 54.1, 48.2, 45.4, 19.9, 14.3; IR (neat) 3032, 2980, 1802, 1713, 1447, 1221, 1152, 1069, 880, 754 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{22}O_4Na_1^+$ ($[M+Na]^+$) 373.1410. Found 373.1411.; HPLC AZ3, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 21.6 min (minor), 24.3 min (major).



3j: The reaction was stirred for 48 h. $[\alpha]_D^{23}$ = –23.0 (*c* = 1.1, $CHCl_3$) for 85% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (1H, m), 7.18-7.14 (2H, m), 7.14-7.08, (3H, m), 6.89 (1H, d, *J* = 7.8 Hz), 6.87-6.83 (2H, m), 5.26 (1H, d, $J_{P\text{-}H}$ = 17.4 Hz), 3.48 (3H, d, $J_{P\text{-}H}$ = 0.9 Hz), 3.45 (3H, d, $J_{P\text{-}H}$ = 0.9 Hz), 3.24 (1H, d, *J* = 13.3 Hz), 3.13 (1H, d, *J* = 13.3 Hz), 3.09 (1H, d, *J* = 13.3 Hz), 2.81 (1H, d, *J* = 13.3 Hz), 1.77 (3H, dd, $J_{P\text{-}H}$ = 3.6 Hz, *J* = 0.9 Hz), ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 157.5 (d, $J_{P\text{-}C}$ = 5.8 Hz), 153.1, 134.1, 130.2, 129.4, 128.2, 128.0, 127.4, 124.8, 124.1, 116.0 (d, $J_{P\text{-}C}$ = 187.7 Hz), 111.0, 54.2, 51.9 (d, $J_{P\text{-}C}$ = 3.9 Hz), 48.8 (d, $J_{P\text{-}C}$ = 24.2 Hz), 45.4, 21.2 (d, $J_{P\text{-}C}$ = 7.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.6; IR (neat) 2951, 2849, 1796, 1773, 1618, 1464, 1248, 1042, 1018, 880 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}O_5P_1Na_1^+$ ($[M+Na]^+$) 409.1175. Found 409.1159.; HPLC OZ3, H/IPA/EtOH = 9:1:1, flow rate = 0.5 mL/min, λ = 210 nm, 45.3 min (minor), 49.2 min (major).



3k: The reaction was stirred for 36 h. $[\alpha]_D^{23}$ = –11.0 (*c* = 0.96, $CHCl_3$) for 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (1H, td, *J* = 7.8, 1.8 Hz), 7.20-7.09 (5H, m), 6.93 (1H, d, *J* = 7.8 Hz), 6.86-6.83 (2H, m), 5.02 (1H, d, *J* = 0.9 Hz), 3.23 (1H, d, *J* = 13.3 Hz), 3.12 (1H, d, *J* = 13.3 Hz), 3.06 (1H, d, *J* = 13.8 Hz), 2.82 (1H, d, *J* = 13.8 Hz), 1.70 (1H, d, *J* = 0.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 158.9, 152.9, 133.8, 130.0, 129.7, 128.2, 127.5, 127.4, 124.3, 124.3, 116.2, 111.2, 100.1, 54.0, 45.3, 45.3, 22.3; IR (neat) 3032, 2922, 2218, 1807, 1788, 1620, 1462, 1225, 1053, 1038, 881 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{17}O_2N_1Na_1^+$ ($[M+Na]^+$) 326.1151. Found 326.1150.; HPLC AD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.6 min (minor), 14.0 min (major).



3l: The reaction was stirred for 36 h. $[\alpha]_D^{22}$ = –19.1 (*c* = 0.97, MeOH) for 45% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.07 (5H, m), 6.87 (1H, d, *J* = 8.7 Hz), 6.85 (1H, d, *J* = 7.8 Hz), 6.85 (1H, d, *J* = 7.8 Hz), 5.42 (1H, s), 3.24 (1H, d, *J* = 13.3 Hz), 3.13 (1H, d, *J* = 13.3 Hz), 2.95 (1H, d, *J* = 13.3 Hz), 2.76 (1H, d, *J* = 13.3 Hz), 2.25 (1H, dq, *J* = 12.8, 7.3 Hz), 2.14 (1H, dq, *J* = 12.8, 7.3 Hz), 1.39 (9H, s), 0.92 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 165.3, 156.7, 153.1, 134.4, 130.2, 129.2, 128.2, 127.3, 124.7, 123.9, 122.1, 111.0, 80. 0 , 54.2, 45.4, 44.5, 28.3, 25.4, 13.0, one peak for aromatic carbon was not found probably due to overlapping; IR (neat) 2976, 2938, 1803, 1755, 1713, 1445, 1261, 1144, 880, 791 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{28}O_4Na_1^+$ ($[M+Na]^+$) 415.1885. Found 415.1878.; HPLC ASH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 8.9 min (minor), 9.9 min (major).

Crystallographic Structure Determination:

Recrystallization of 3g, 3j and 3k: A single crystal of **3g** was obtained from hexane solvent at 0 °C, **3j** was obtained from hexane/$CHCl_3$ solvent system at 0 °C and **3k** was obtained from Et_2O solvent at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 123 K on a Brucker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXTL.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. The crystallographic data are summarized in the following table.

Table S1. Crystal data and structure refinement for **3g**

Empirical formula	C24 H25 Cl O4	
Formula weight	412.89	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.4505(14) Å	α= 90°.

[3] Sheldrick, G. M. SHELXTL 5.1, Bruker AXS Inc., Madison, Wisconsin, 1997.

	b = 7.7509(17) Å	β= 90°.
	c = 42.666(9) Å	γ = 90°.
Volume	2133.2(8) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.206 mm^{-1}	
F(000)	872	
Crystal size	0.50 x 0.45 x 0.40 mm^3	
Theta range for data collection	0.954 to 28.317°.	
Index ranges	-8<=h<=8, -9<=k<=10, -56<=l<=48	
Reflections collected	15427	
Independent reflections	5294 [R(int) = 0.0358]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5294 / 0 / 266	
Goodness-of-fit on F^2	0.719	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1125	
R indices (all data)	R1 = 0.0506, wR2 = 0.1254	
Absolute structure parameter	0.03(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.391 and -0.291 $e.Å^{-3}$	

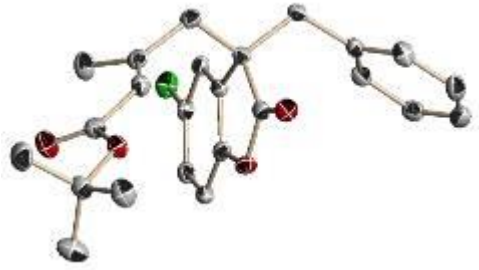


Figure S1. Molecular structure of **3g**. All calculated hydrogen atoms are omitted for clarity. green = chlorine, red = oxygen, black = carbon.

Table S2. Crystal data and structure refinement for **3j**

Empirical formula	C21 H23 O5 P	
Formula weight	386.36	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.647(3) Å	α= 90°.
	b = 9.403(4) Å	β= 90°.
	c = 24.219(9) Å	γ = 90°.

Volume	1969.0(13) $Å^3$
Z	4
Density (calculated)	1.303 Mg/m^3
Absorption coefficient	0.168 mm^{-1}
F(000)	816
Crystal size	0.30 x 0.25 x 0.21 mm^3
Theta range for data collection	2.324 to 28.273°.
Index ranges	-7<=h<=11, -12<=k<=10, -29<=l<=32
Reflections collected	13602
Independent reflections	4824 [R(int) = 0.0443]
Completeness to theta = 25.242°	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4824 / 0 / 247
Goodness-of-fit on F^2	1.184
Final R indices [I>2sigma(I)]	R1 = 0.0789, wR2 = 0.2183
R indices (all data)	R1 = 0.1131, wR2 = 0.2892
Absolute structure parameter	0.05(5)
Extinction coefficient	n/a
Largest diff. peak and hole	1.425 and -1.438 $e.Å^{-3}$

Figure S2. Molecular structure of **3j**. All calculated hydrogen atoms are omitted for clarity. Purple = phosphorus, red = oxygen, black = carbon.

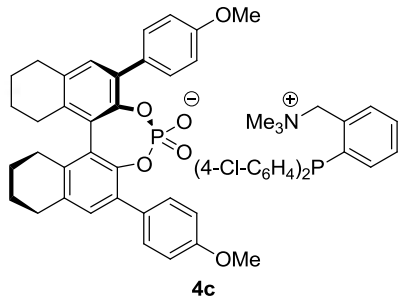
Table S3. Crystal data and structure refinement for **3k**

Empirical formula	C20 H17 N O2	
Formula weight	303.35	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 6.6395(10) Å	α= 90°.
	b = 15.610(2) Å	β= 91.710(3)°.
	c = 7.8147(12) Å	γ = 90°.
Volume	809.6(2) $Å^3$	
Z	2	

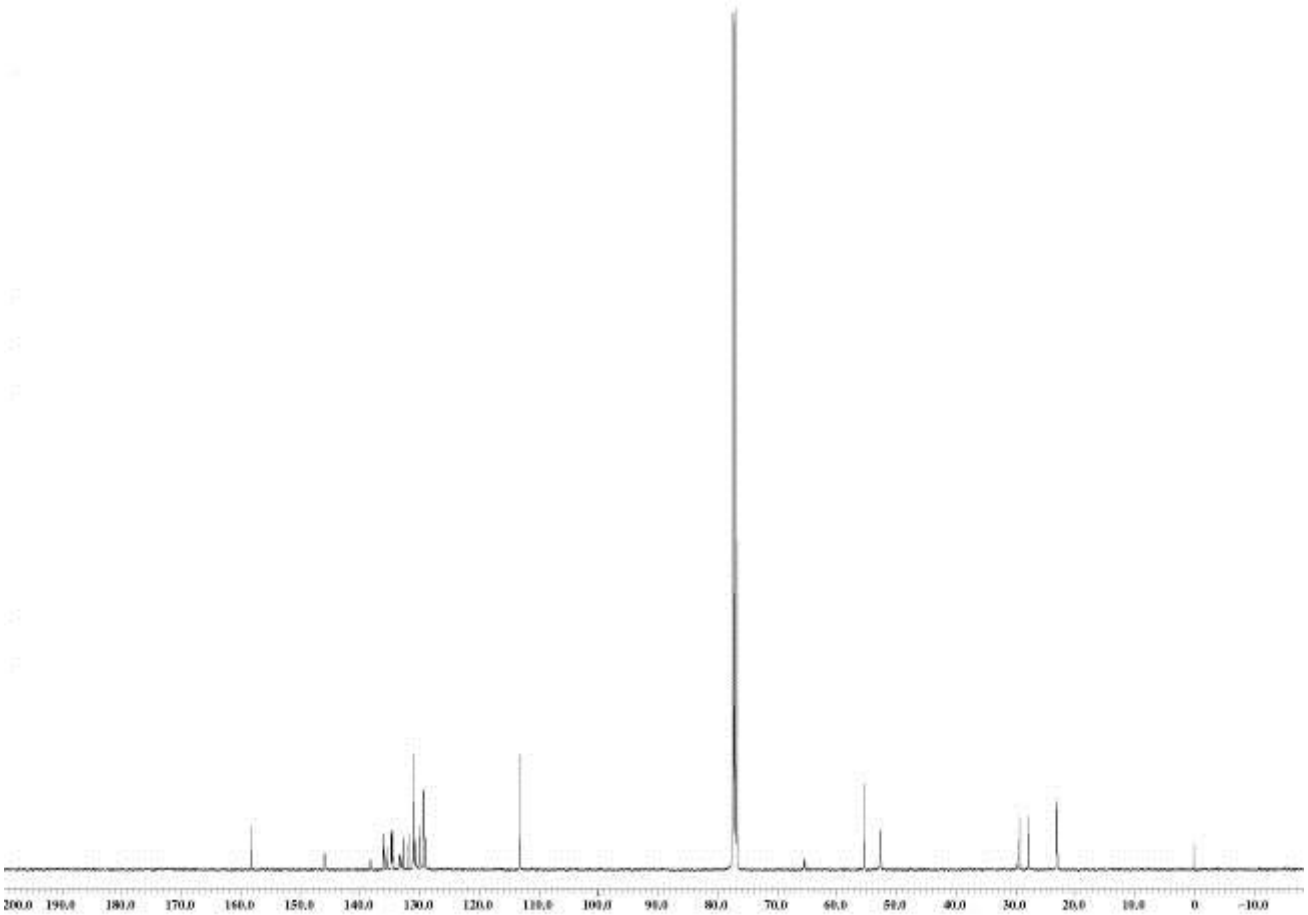
Density (calculated)	1.244 Mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	320
Crystal size	0.5 x 0.45 x 0.4 mm^3
Theta range for data collection	2.608 to 28.270°.
Index ranges	-6<=h<=8, -20<=k<=17, -10<=l<=10
Reflections collected	5814
Independent reflections	3186 [R(int) = 0.0243]
Completeness to theta = 25.242°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3186 / 1 / 209
Goodness-of-fit on F^2	0.962
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1204
R indices (all data)	R1 = 0.0504, wR2 = 0.1233
Absolute structure parameter	0.1(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.295 and -0.232 $e.Å^{-3}$

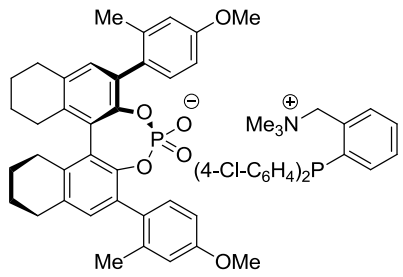
Figure S3. Molecular structure of **3k**. All calculated hydrogen atoms are omitted for clarity. blue = nitrogen, red = oxygen, black = carbon.

Copies of ^{1}H and ^{13}C NMR Spectra:



4c





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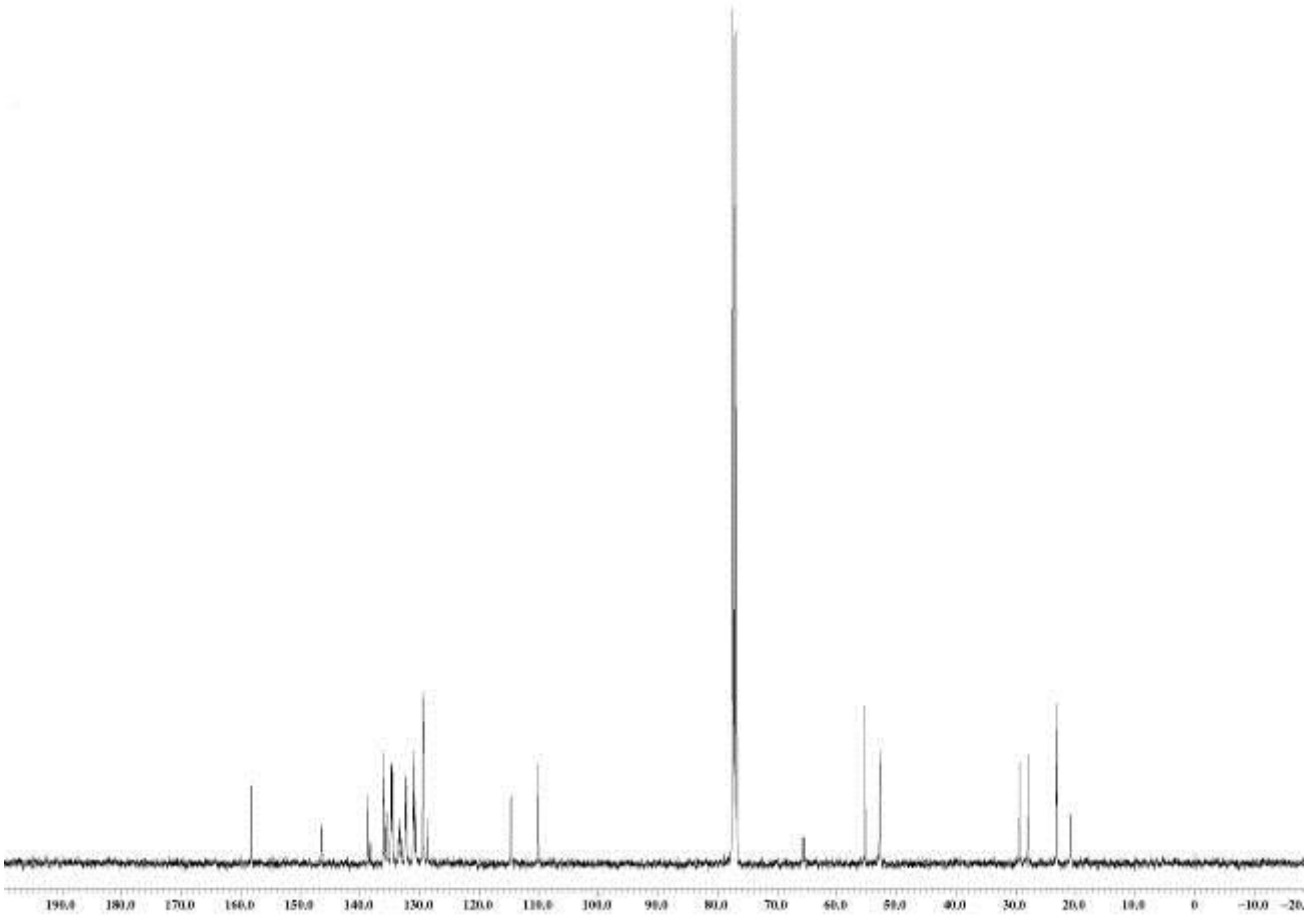

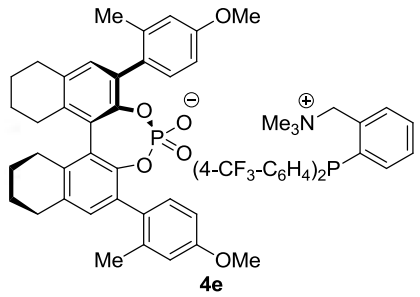
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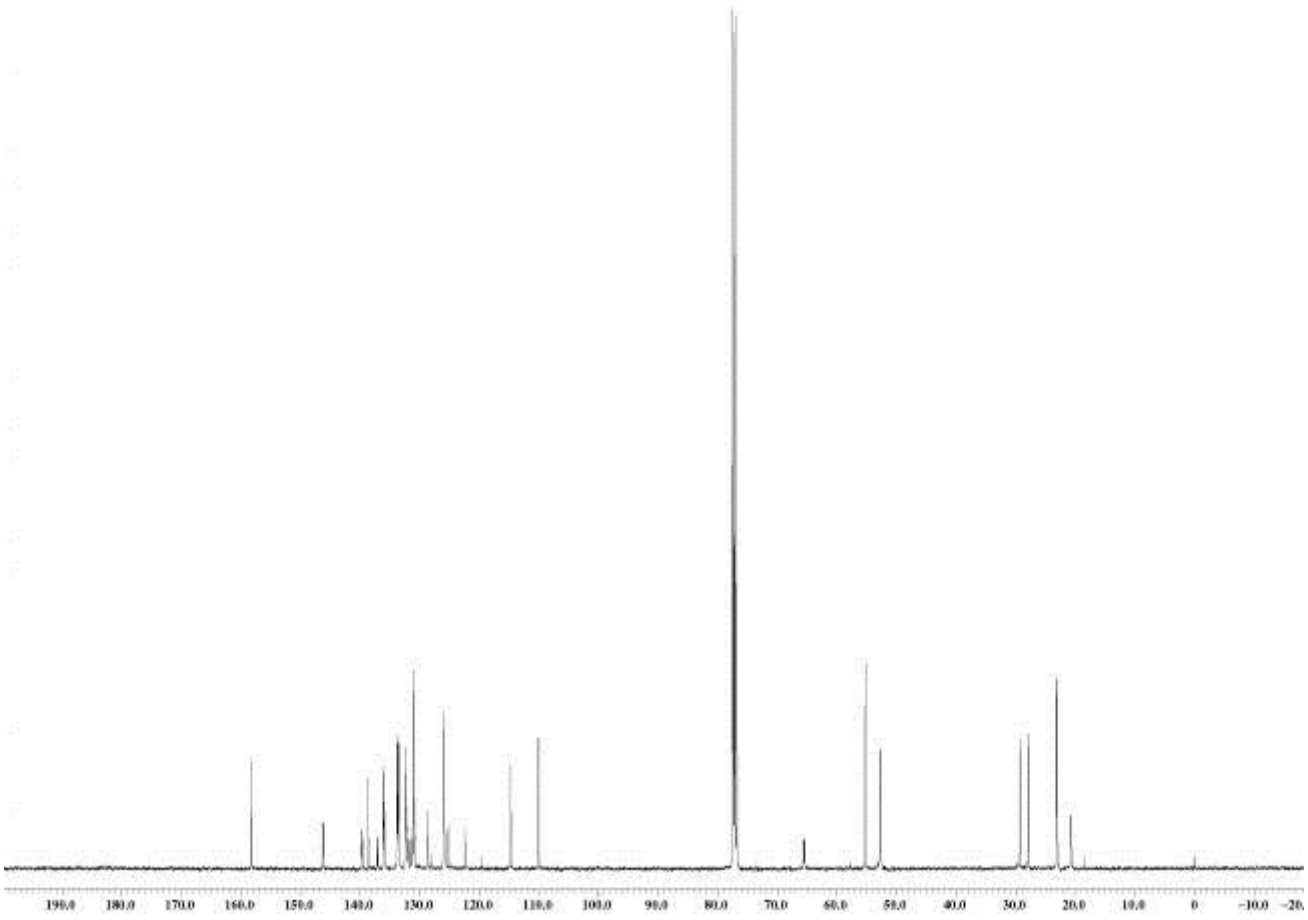
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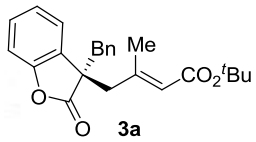
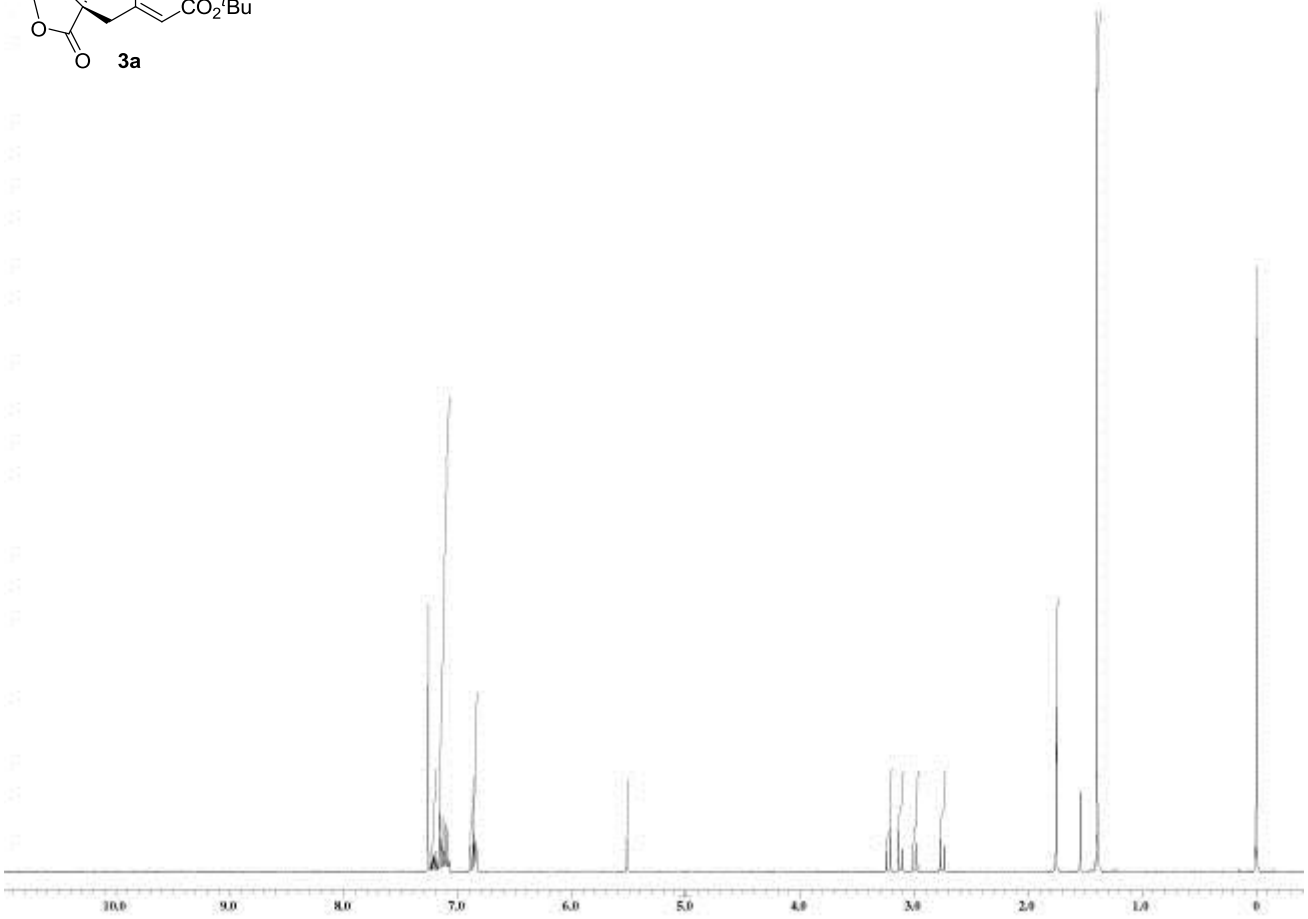
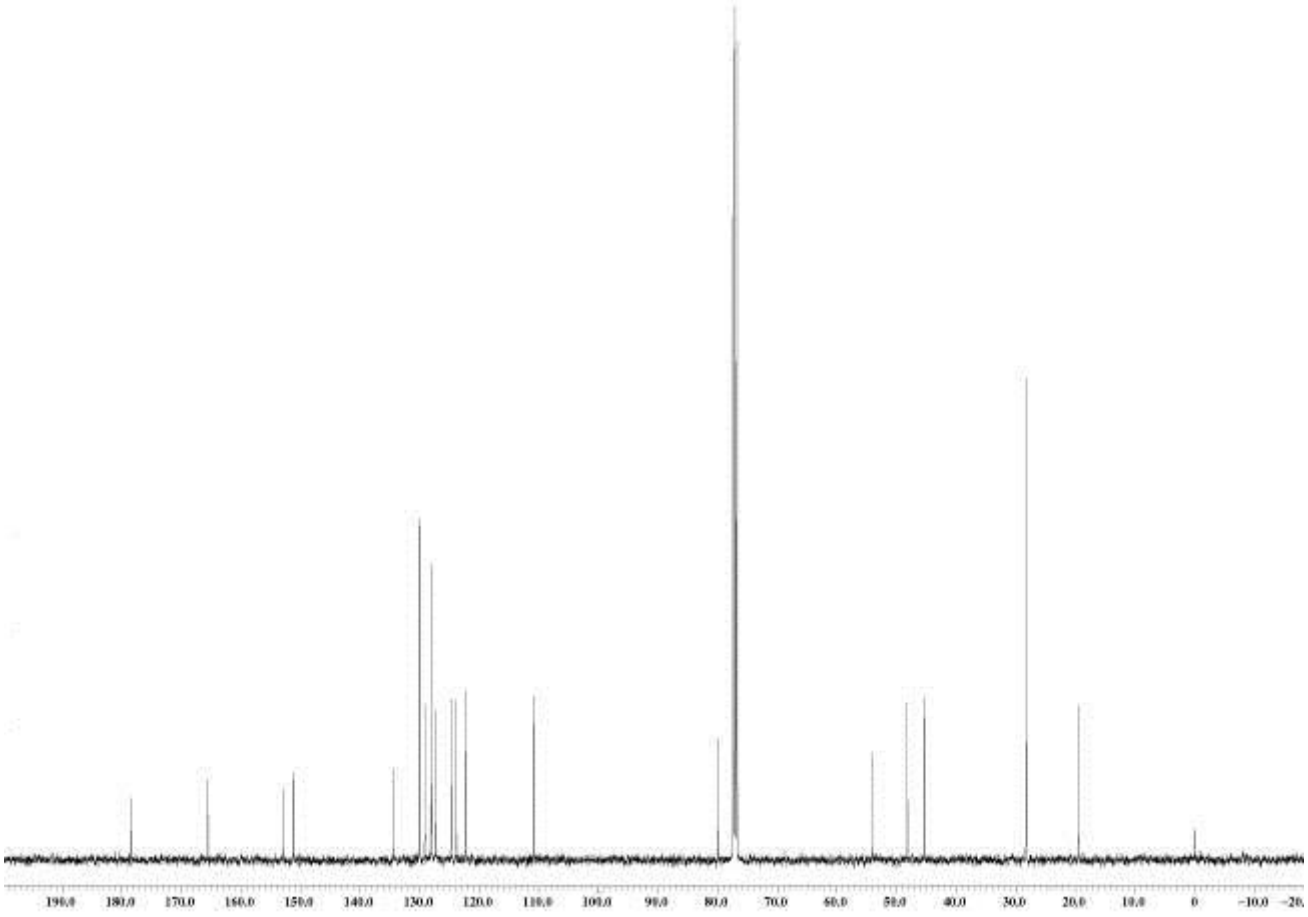
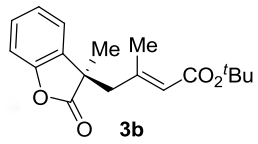


3a



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3b

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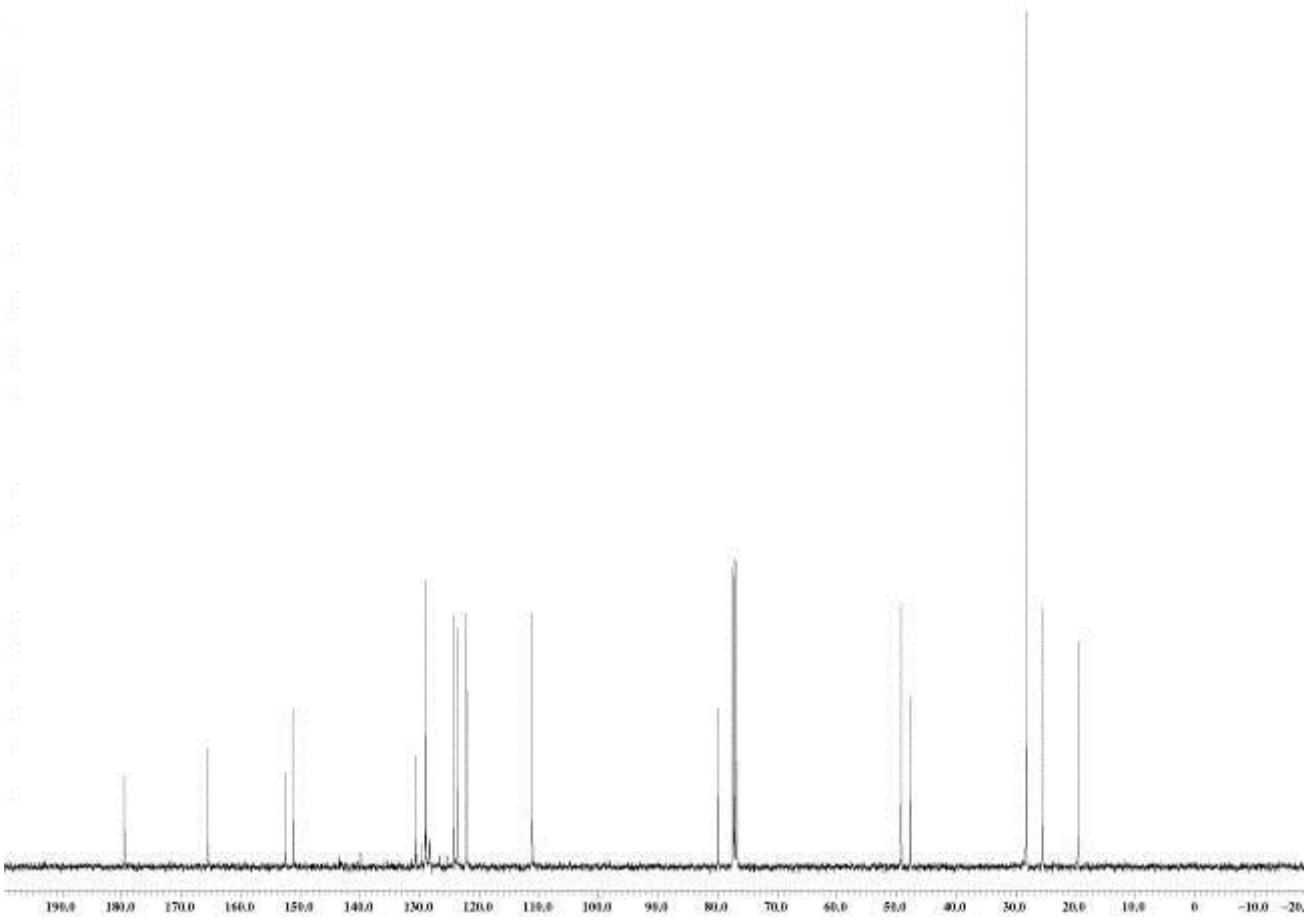
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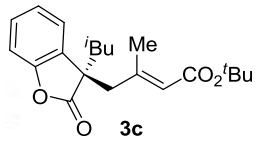

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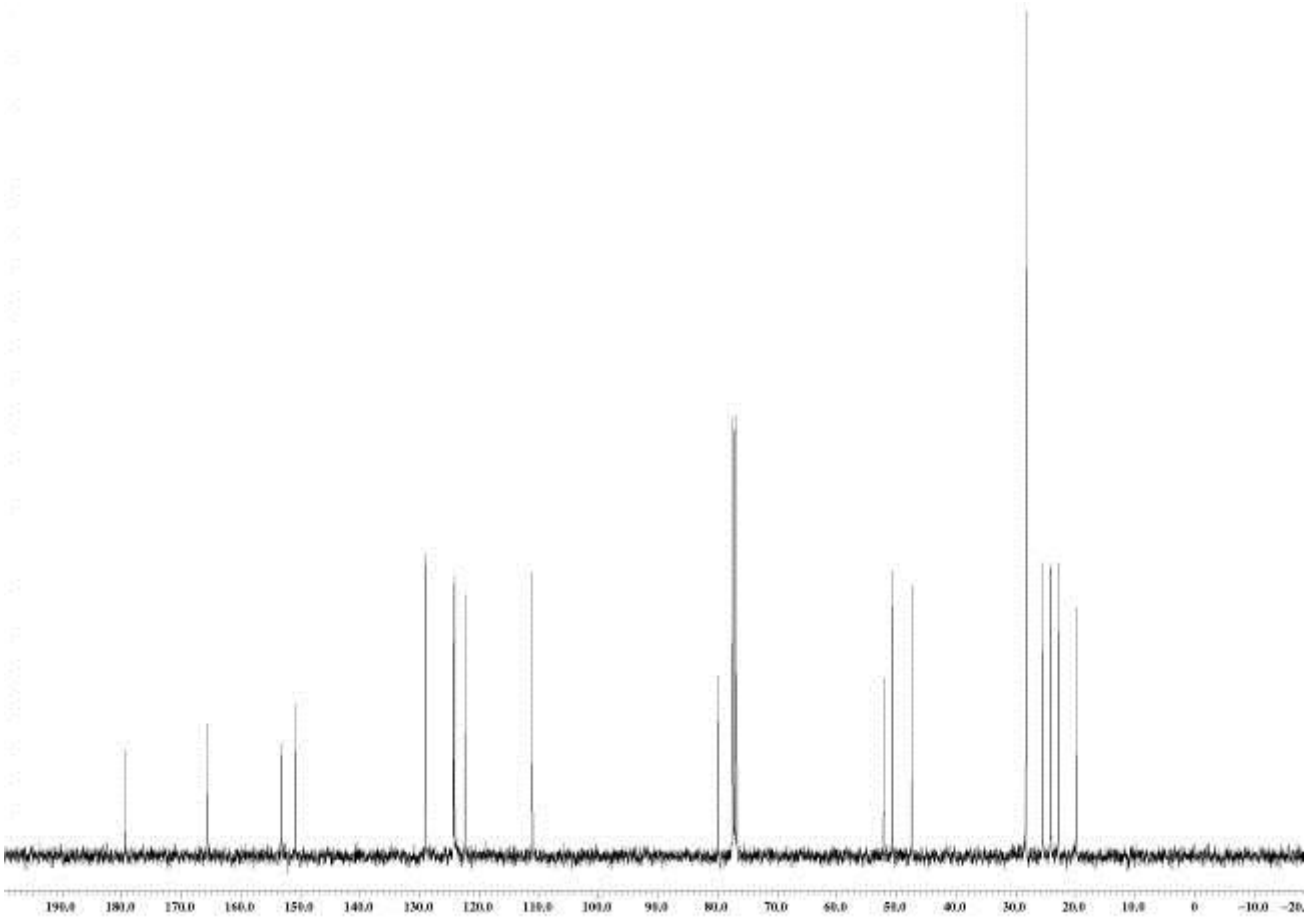

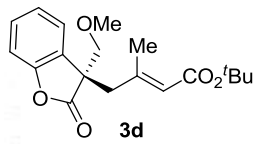

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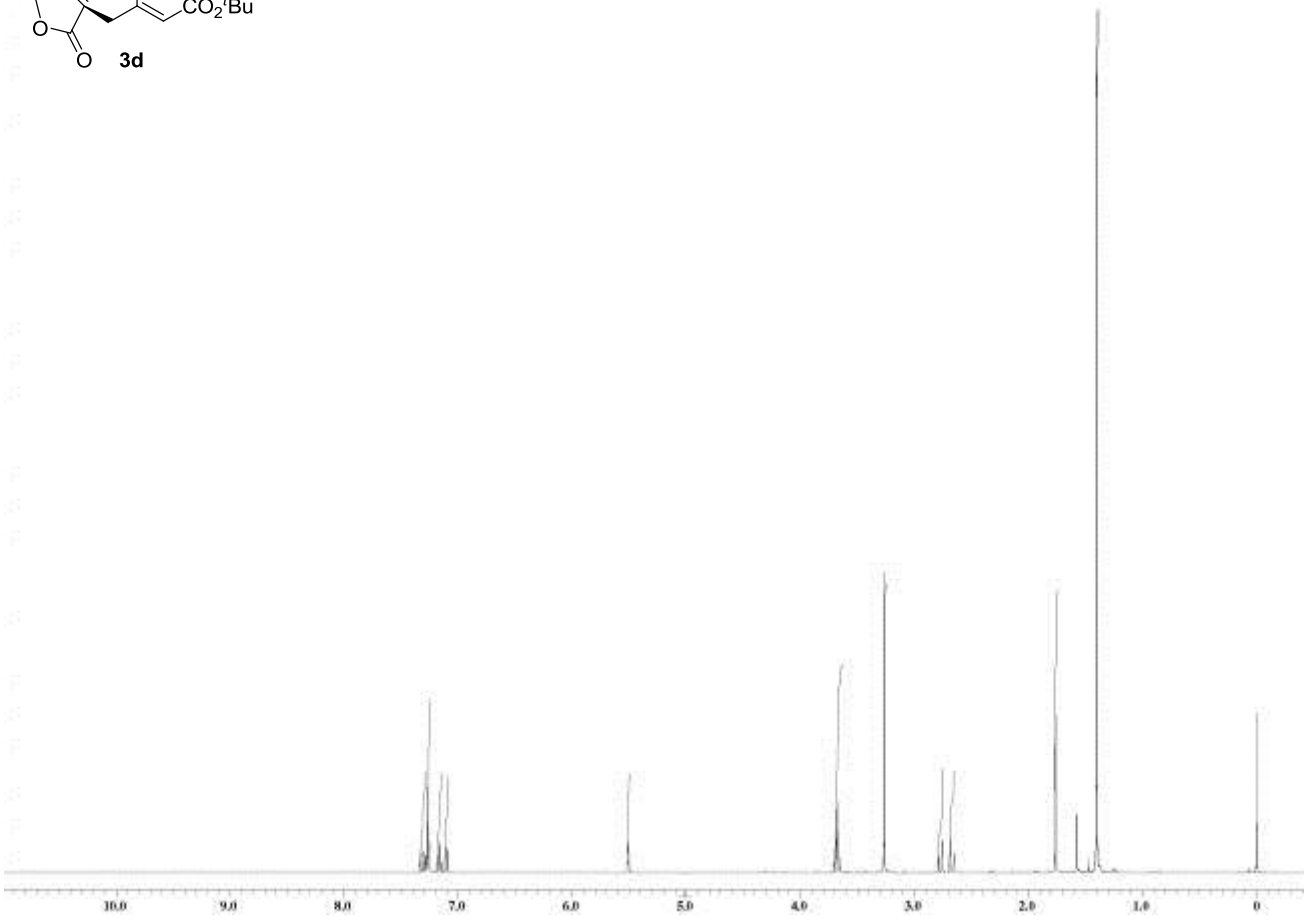

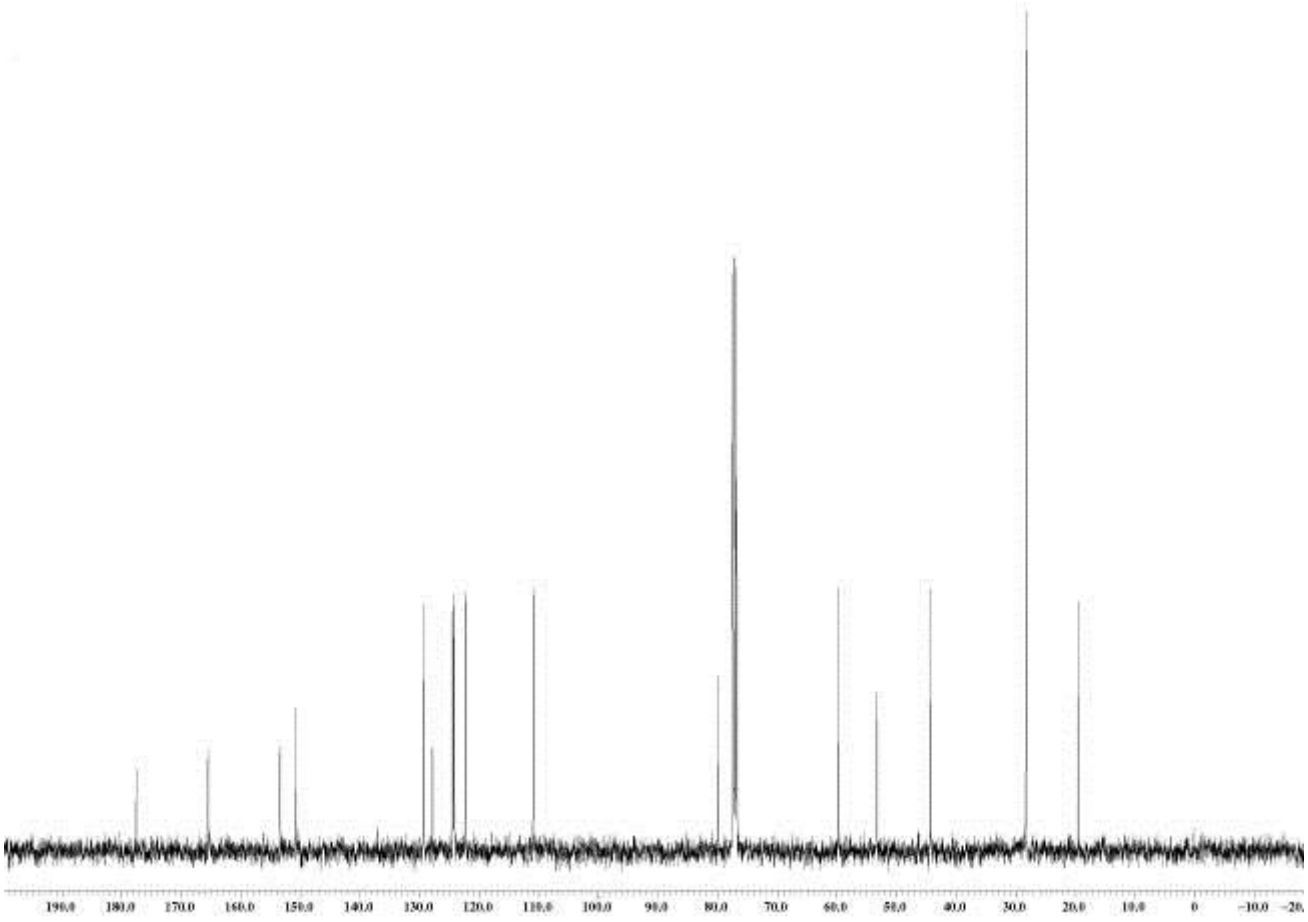

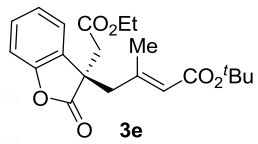
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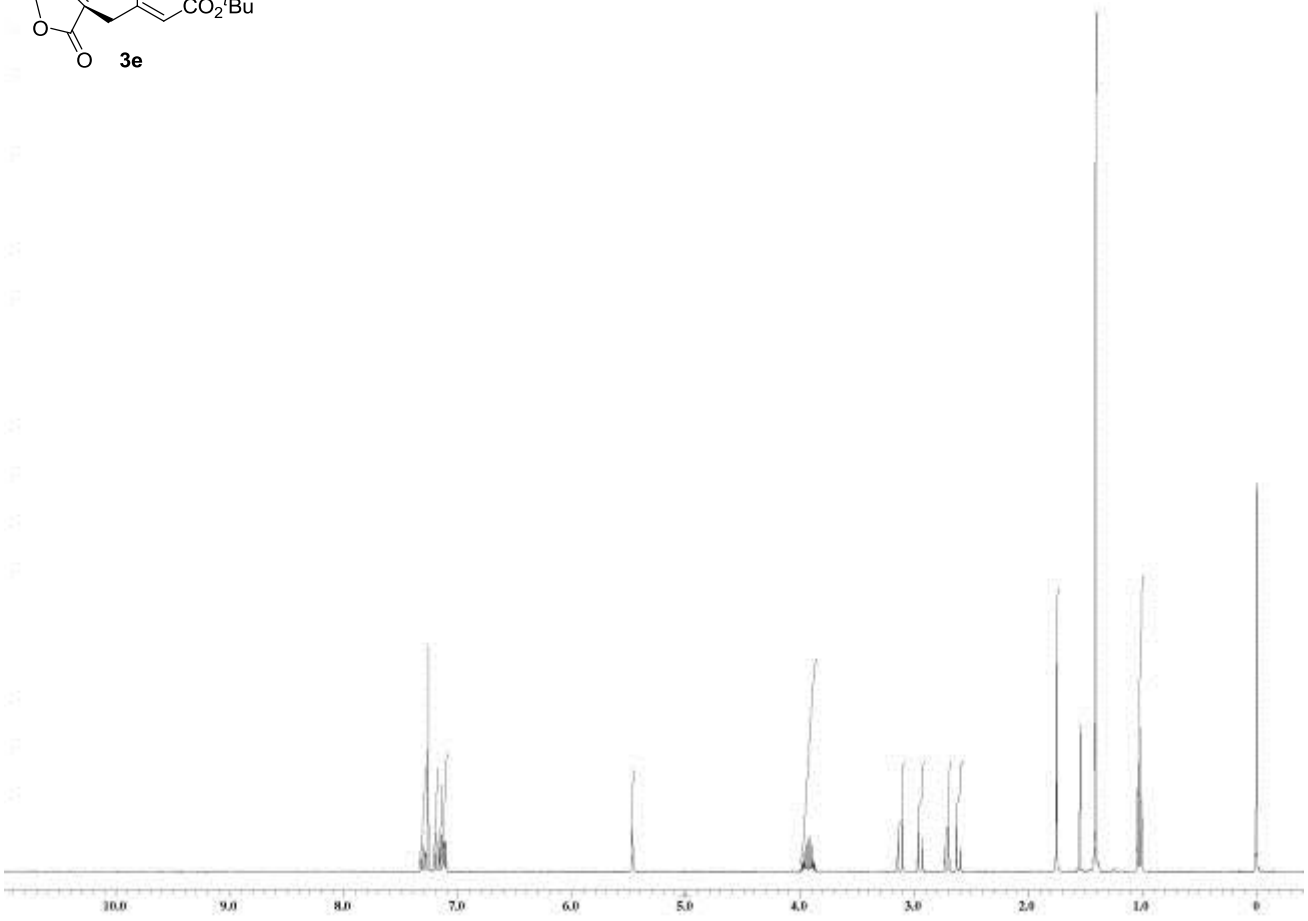
3e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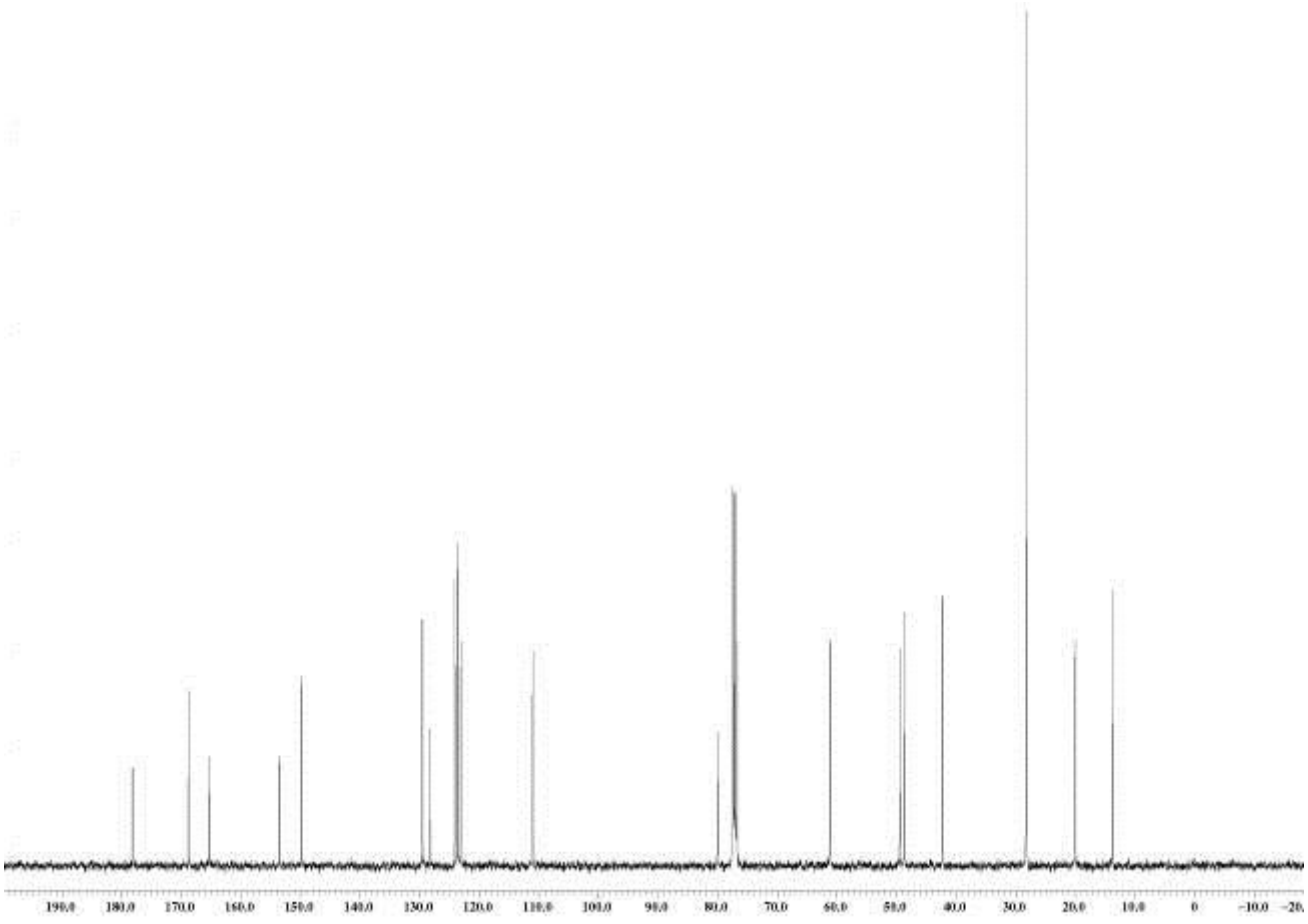
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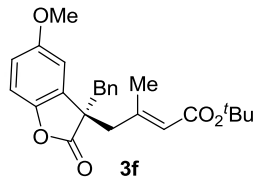

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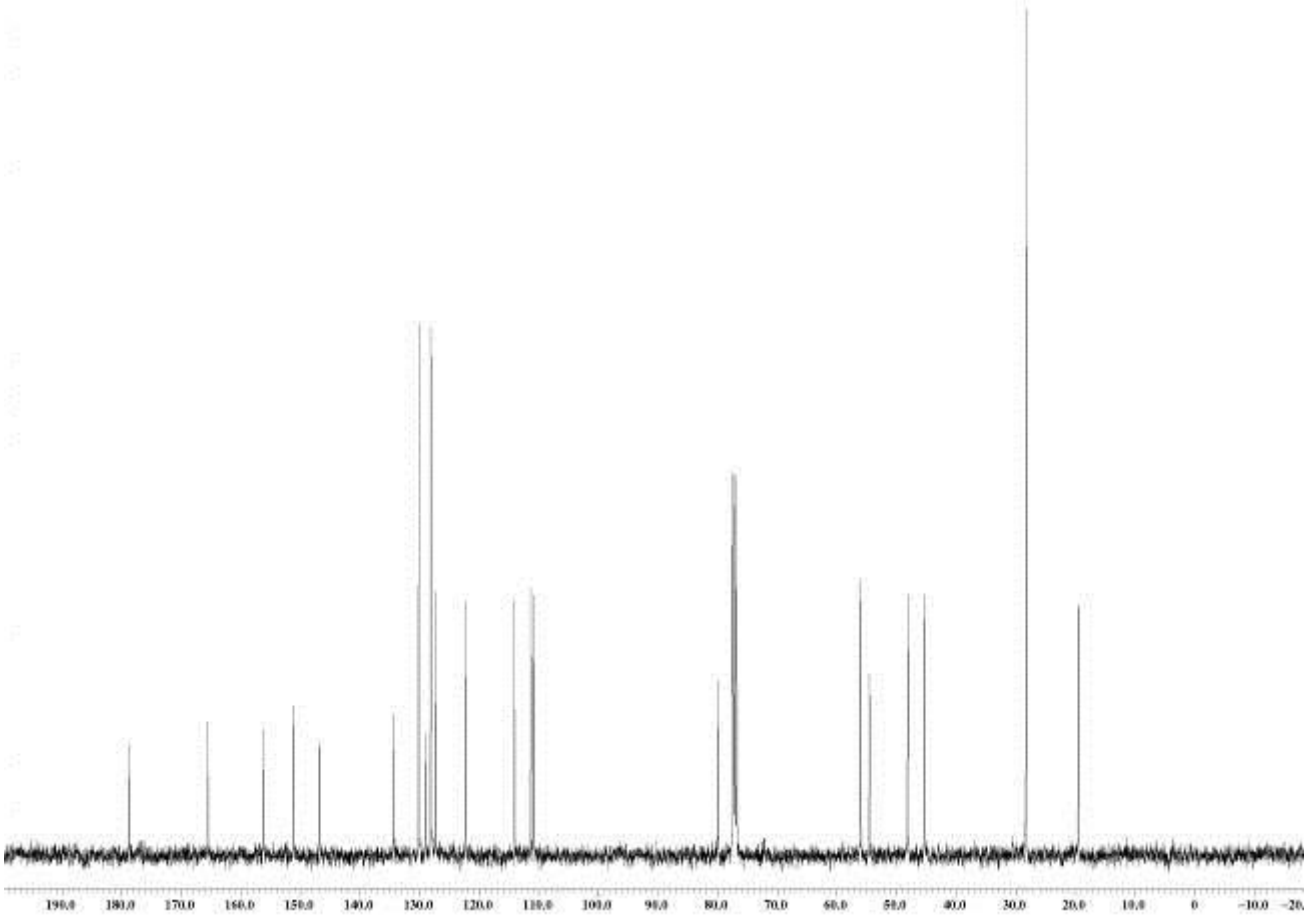

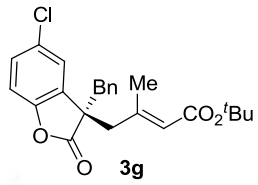
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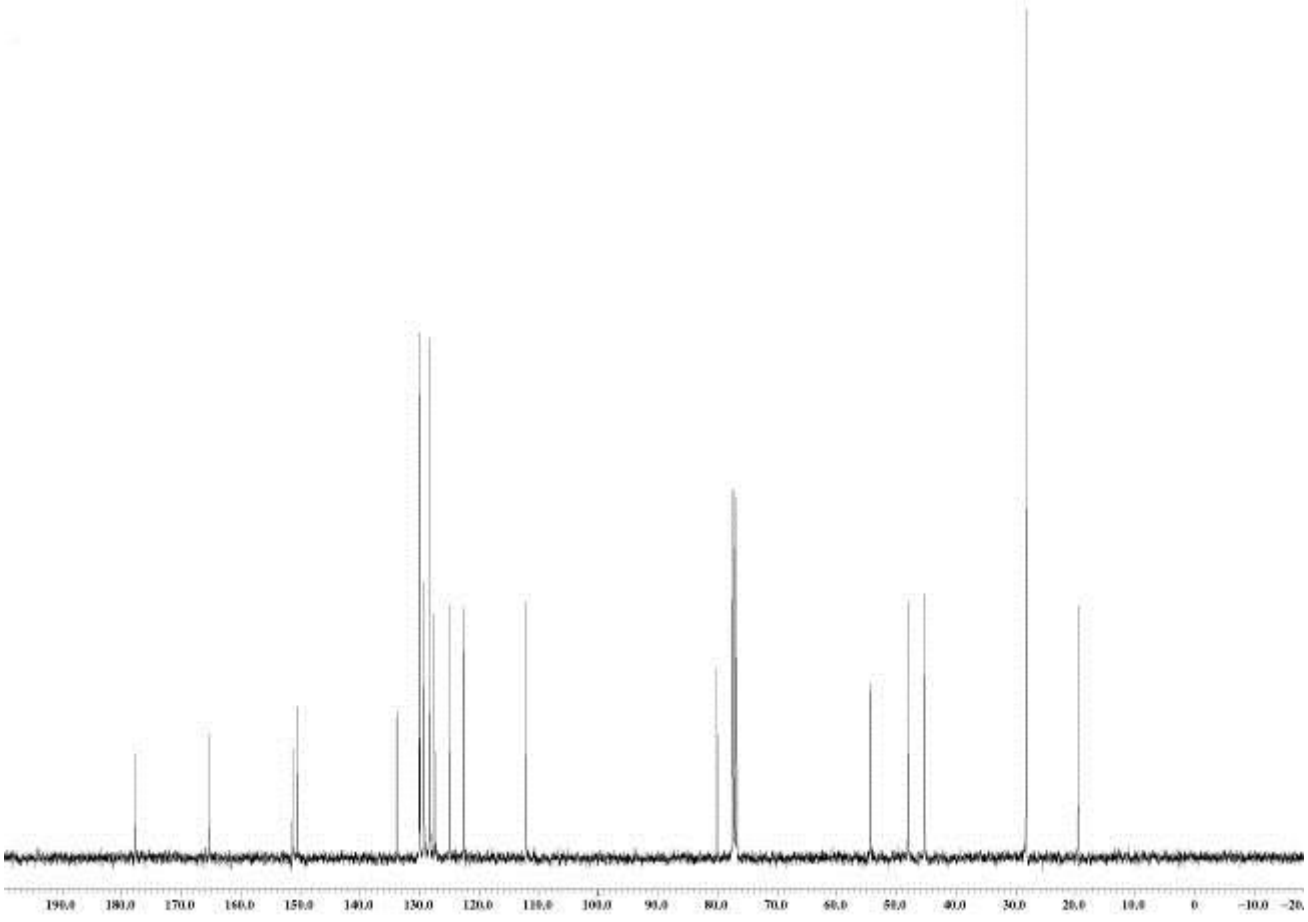
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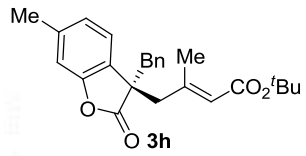

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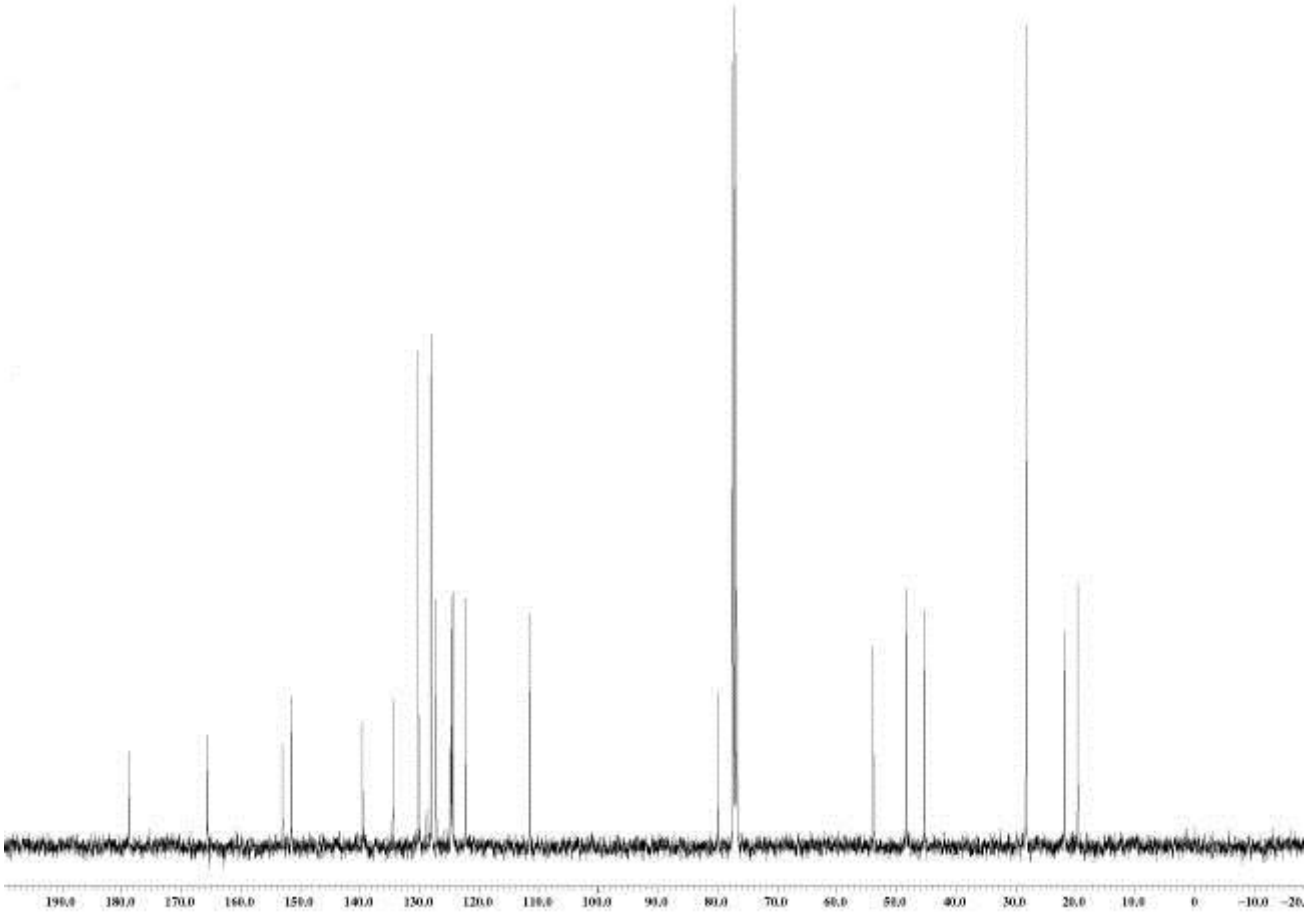

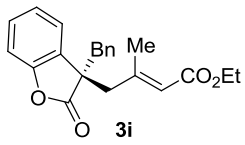

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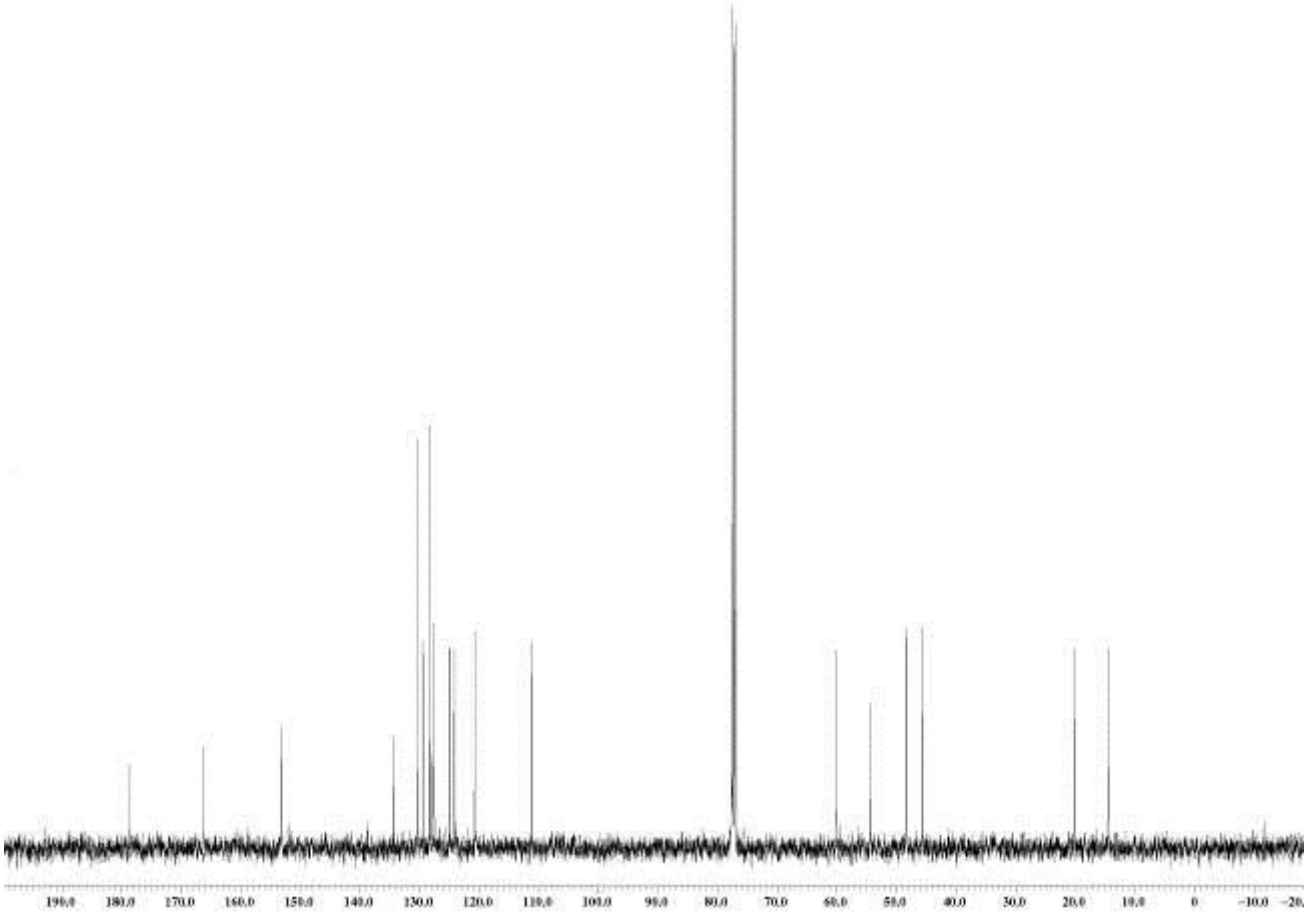

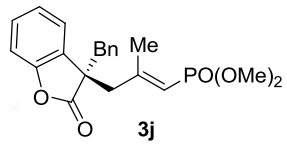
Bn
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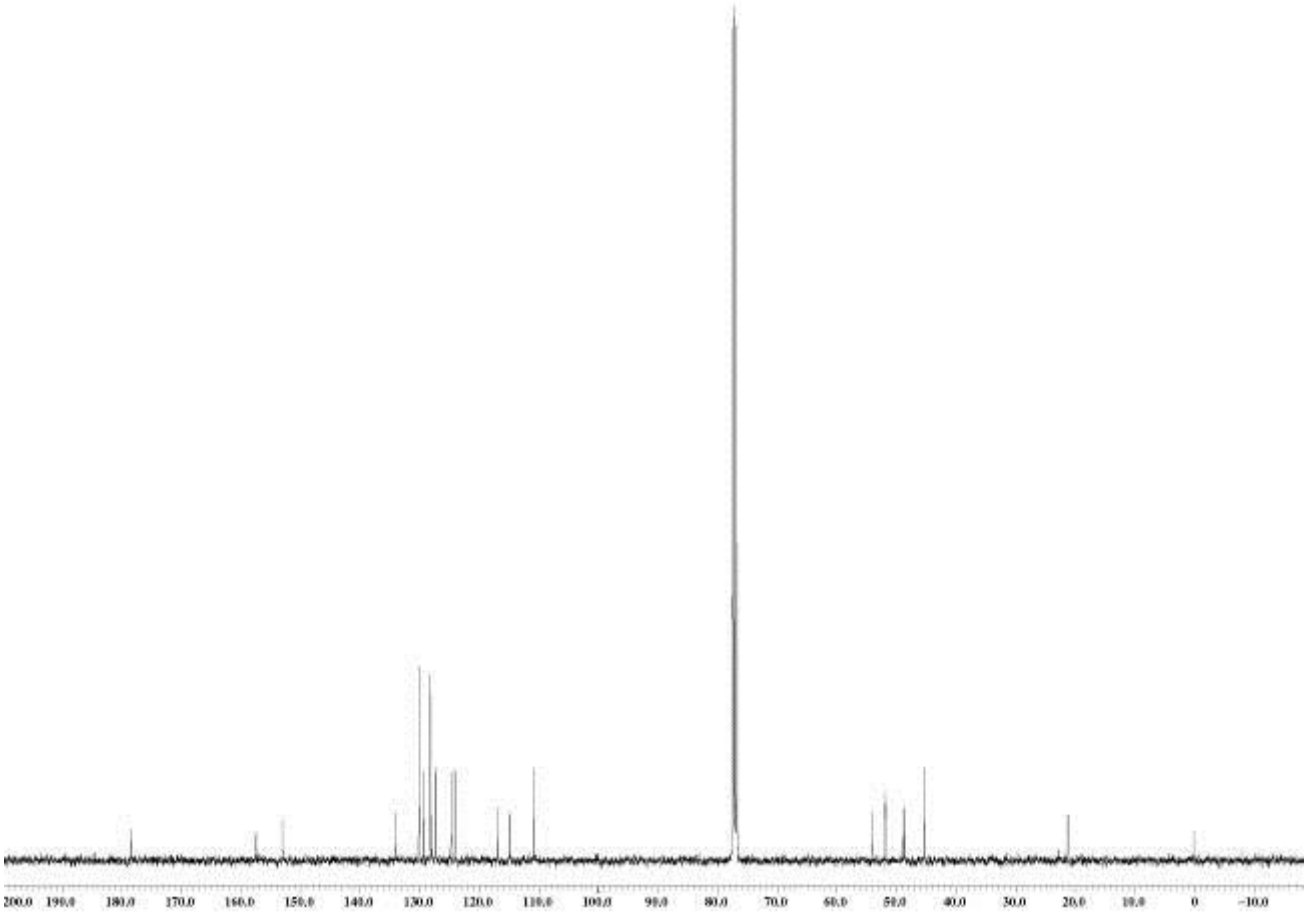
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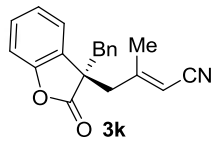

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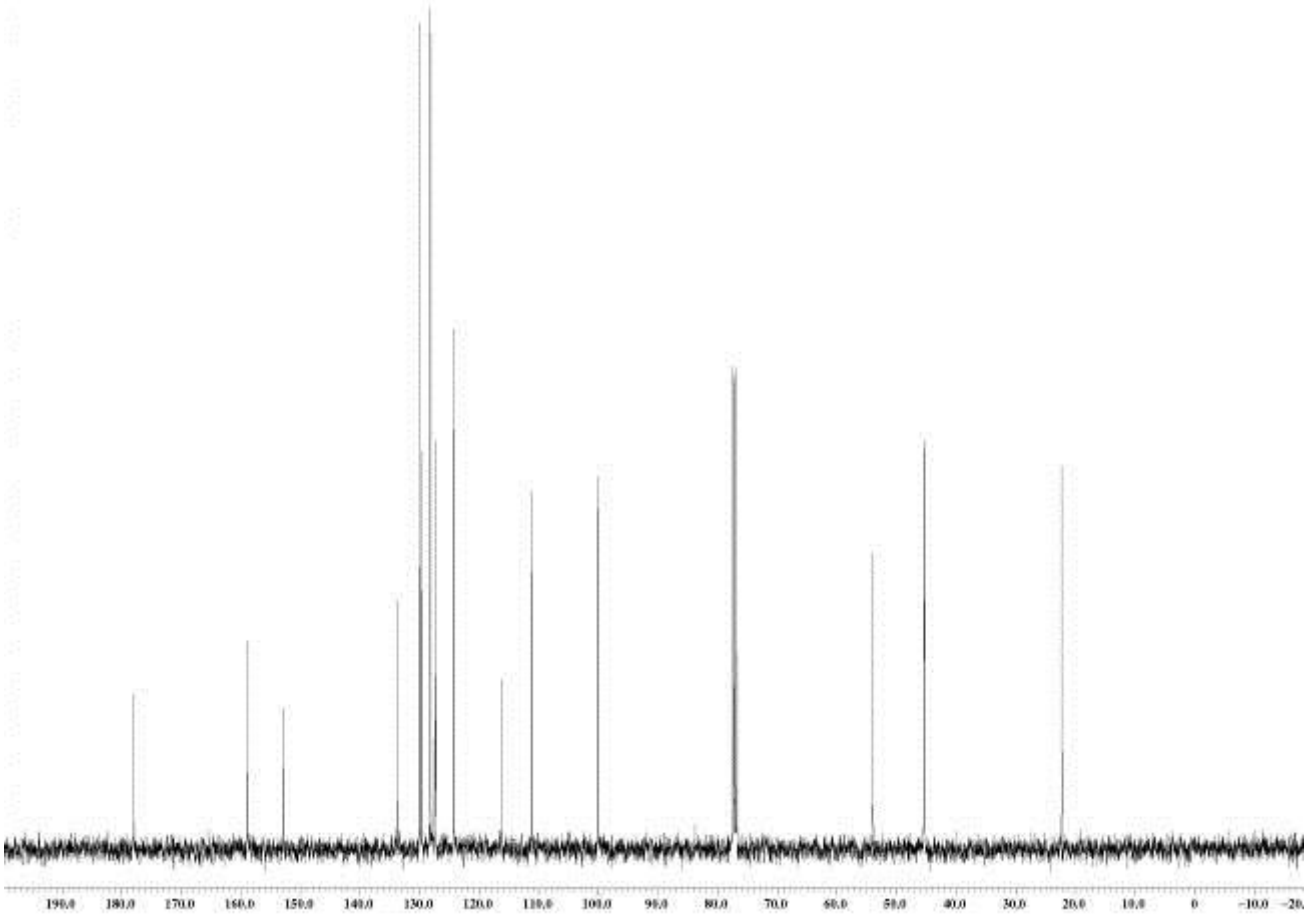

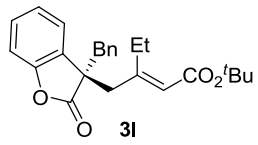
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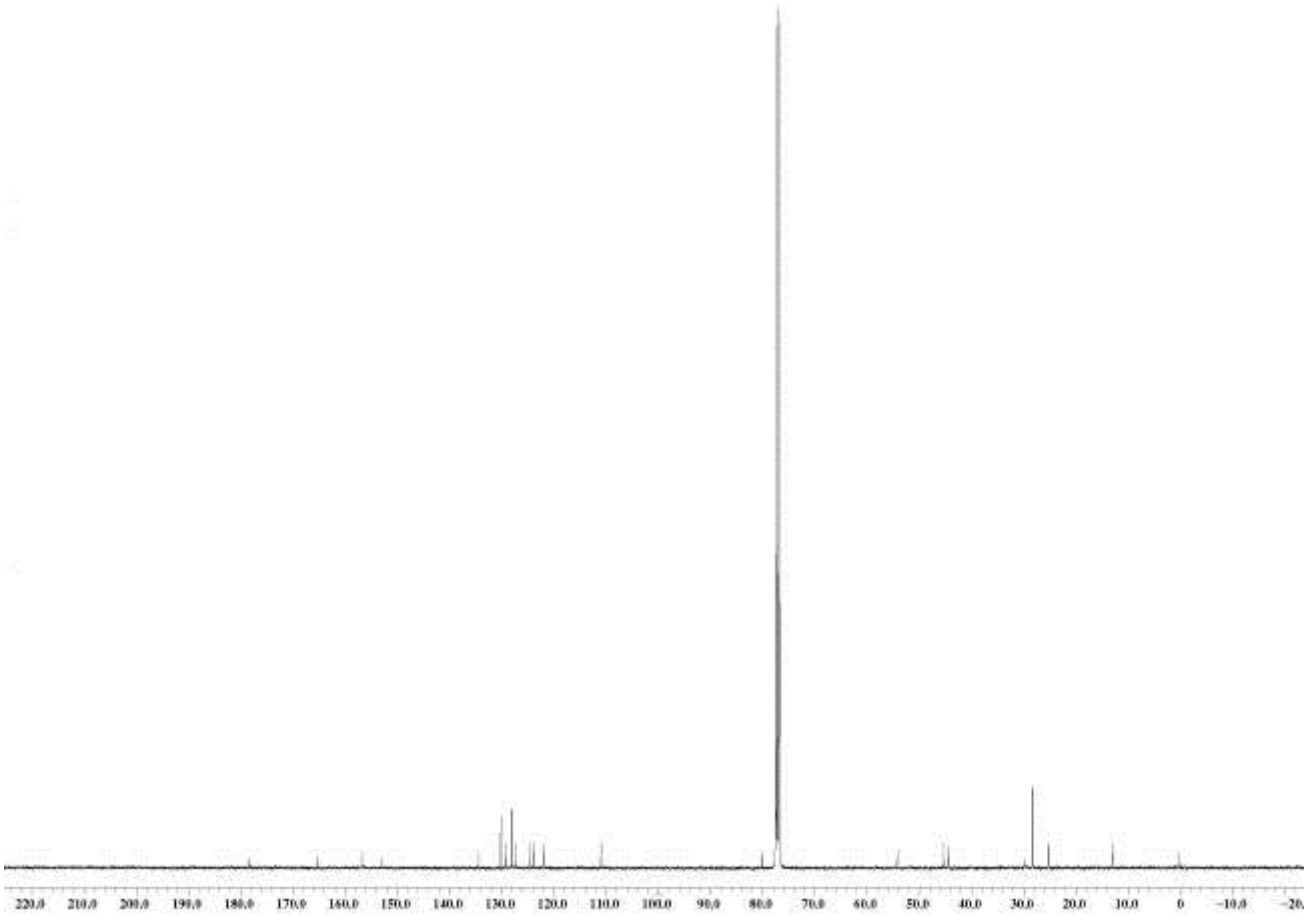
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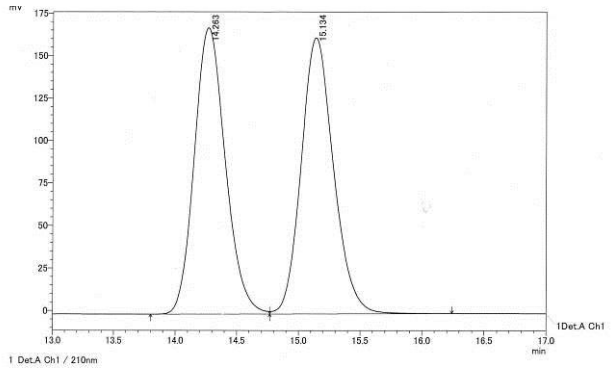
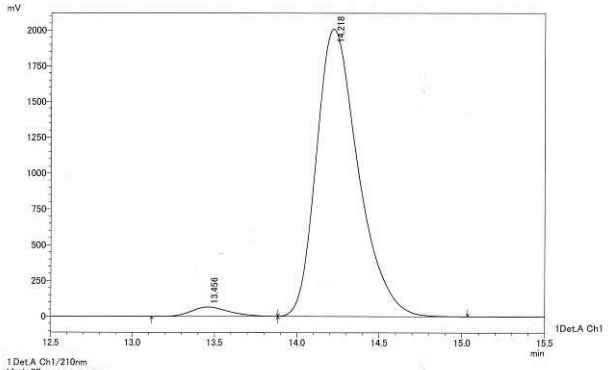
Copies of HPLC Chromatograms:

3a

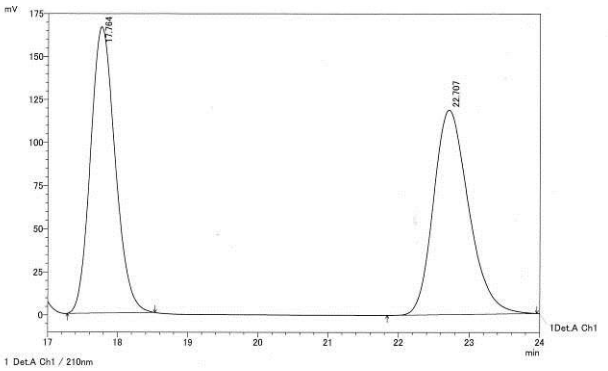


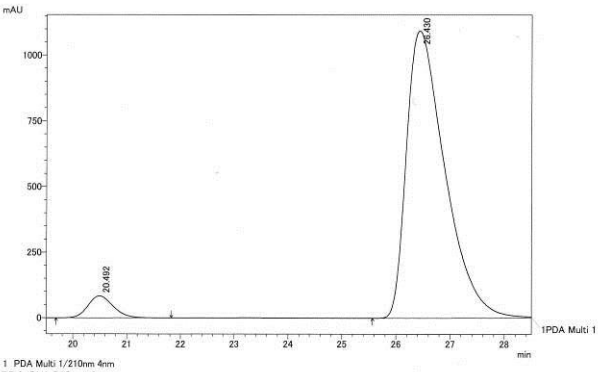


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	13.456	2.814
2	14.218	97.186
合計		100.000

3c

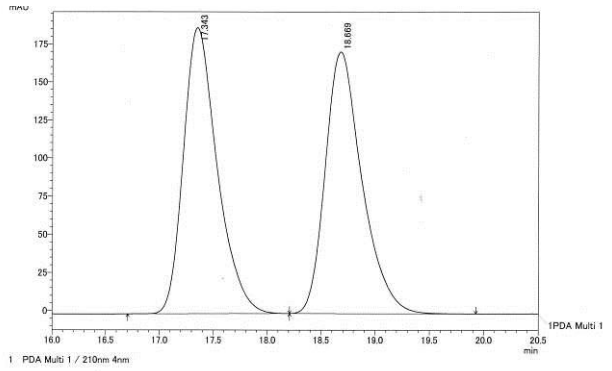


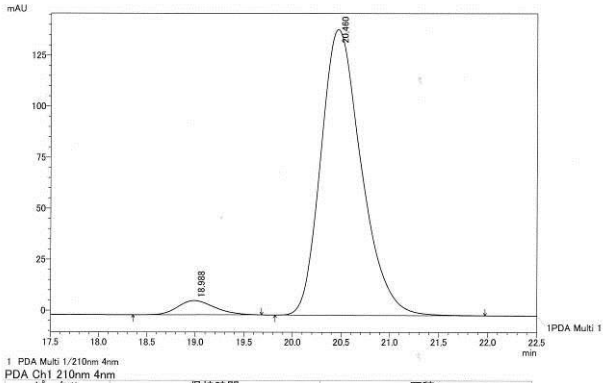


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	20.492	4.826
2	26.430	95.174
合計		100.000

3b

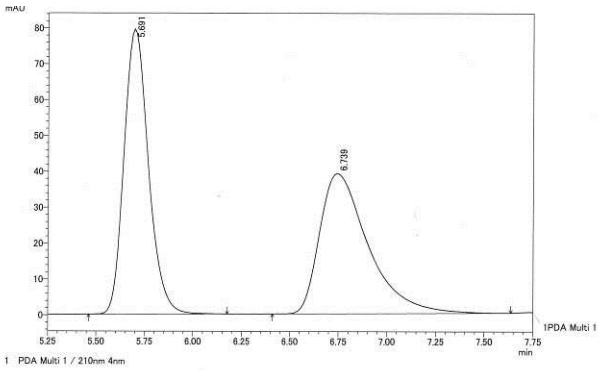


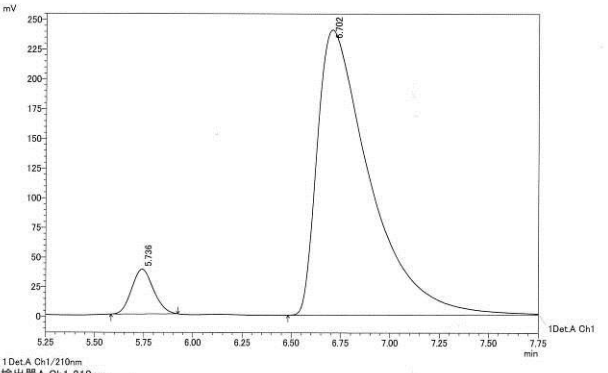


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	18.988	4.325
2	20.460	95.675
合計		100.000

3d

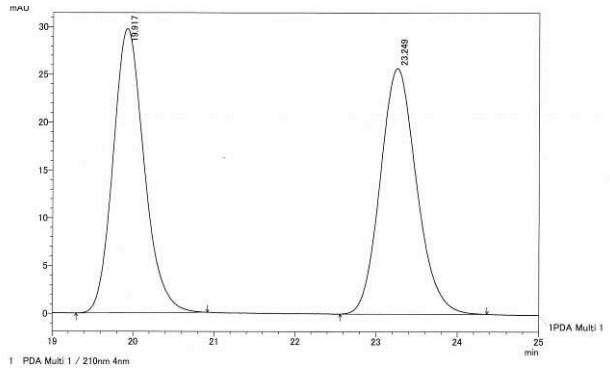


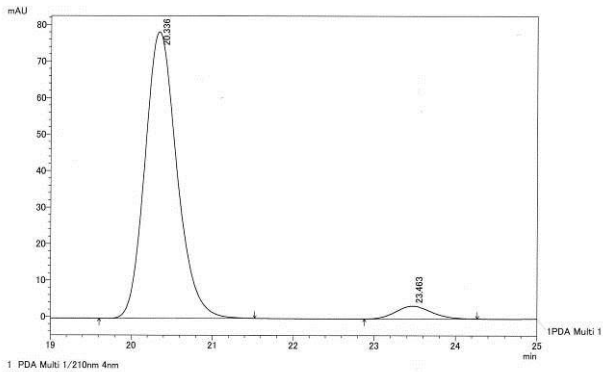


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	5.736	6.182
2	6.702	93.818
合計		100.000

3e

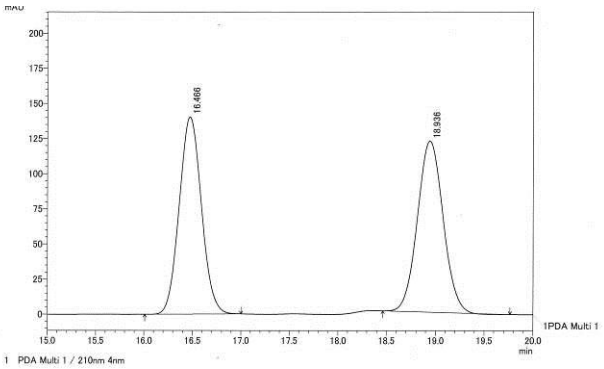


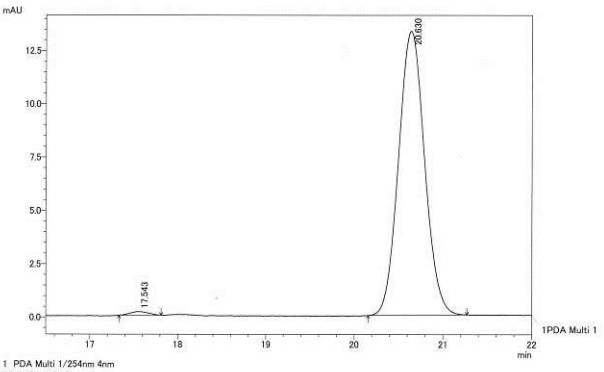


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	20.336	95.127
2	23.463	4.873
合計		100.000

3g

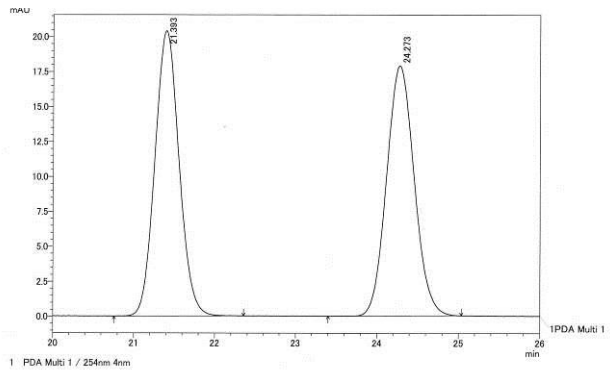


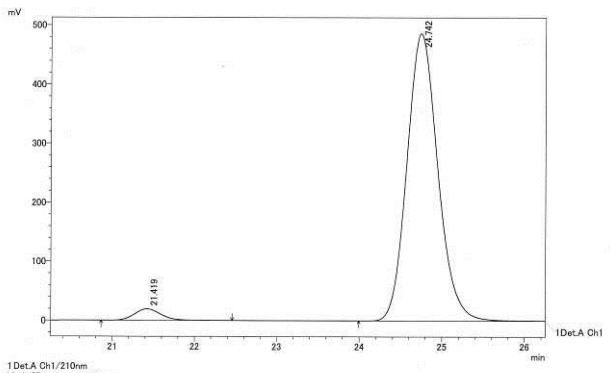


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	17.555	1.415
2	20.630	98.585
合計		100.000

3f

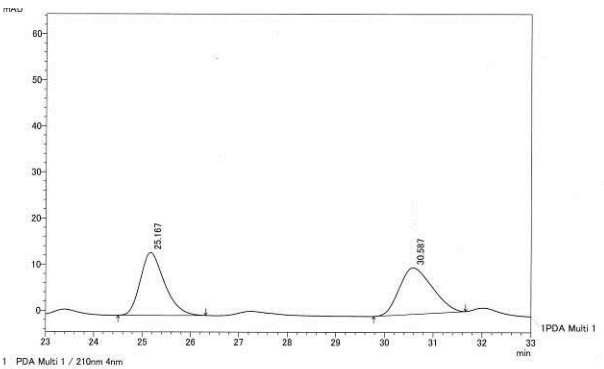


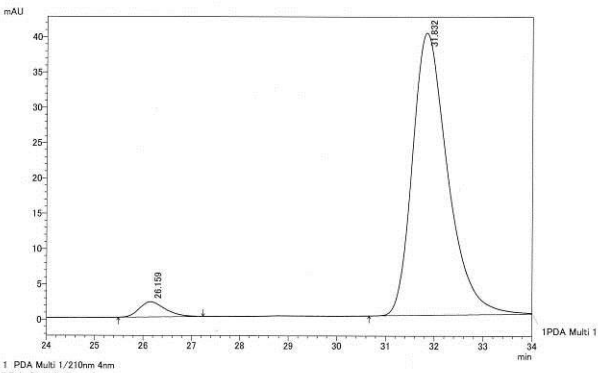


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	21.419	3.346
2	24.742	96.654
合計		100.000

3h

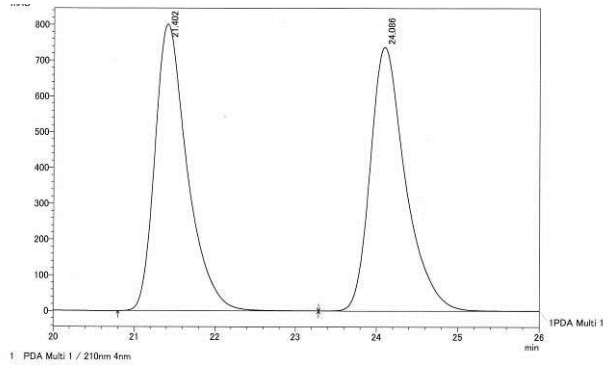


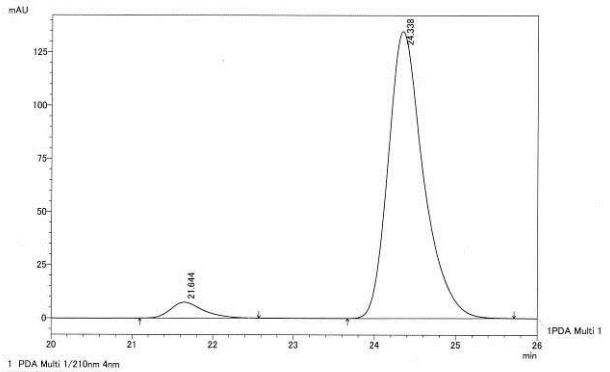


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	26.159	3.829
2	31.832	96.171
合計		100.000

3i

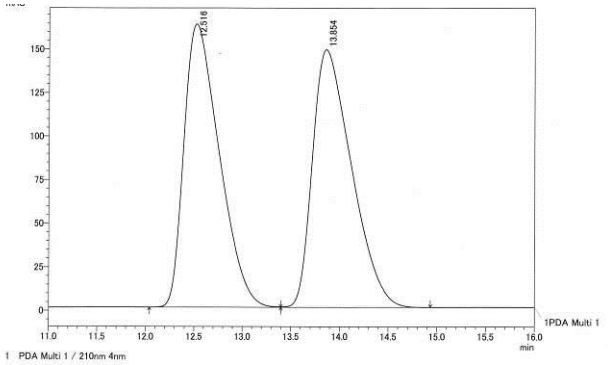


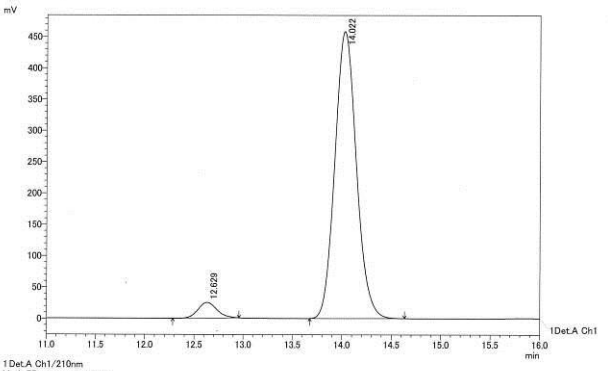


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	21.644	4.873
2	24.338	95.127
合計		100.000

3k

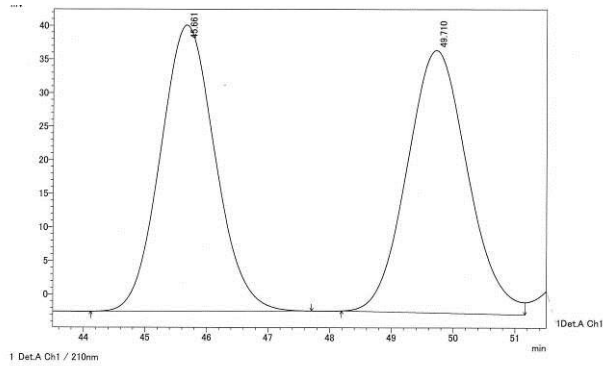


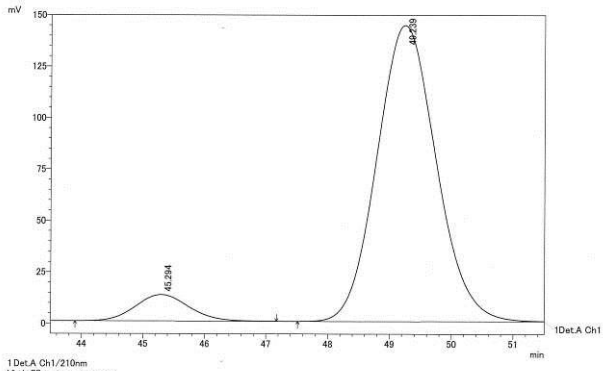


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	12.629	4.596
2	14.022	95.404
合計		100.000

3j

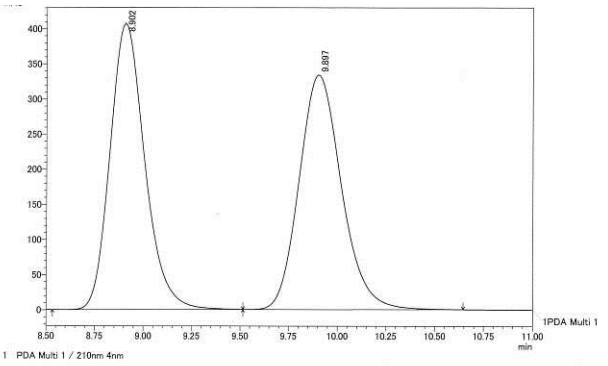


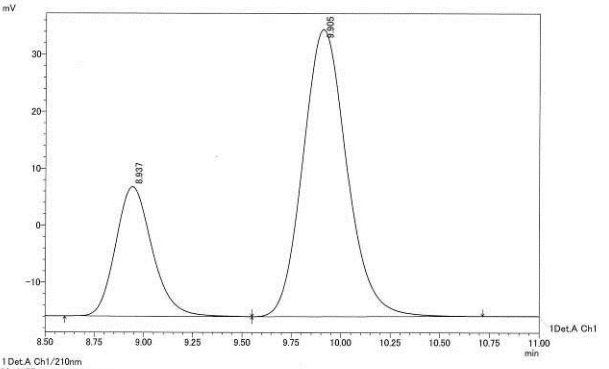


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	45.294	7.533
2	49.239	92.467
合計		100.000

3l





検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	8.937	27.415
2	9.905	72.585
合計		100.000