Electronic Supplementary Information for

N-Sulfonyl α-Imino Ester-Derived Chiral Oxaziridines: Catalytic Asymmetric Synthesis and Application as a Modular Chiral Organic Oxidant

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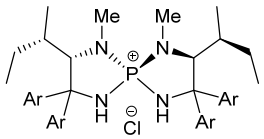
General Information: Infrared spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer or JEOL JNM-ECA600 (600 MHz). Chemical shifts are reported in ppm from tetramethylsilane (0.00 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer or JEOL JNM-ECA600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance ($CDCl_3$: 77.16 ppm). ^{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. ^{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. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.) or silica gel 60 (spherical, 40-50 μm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALCEL OD-3 (OD-3), CHIRALPAK AD-3 (AD-3), CHIRALPAK AY-3 (AY-3), CHIRALCEL OX-3 (OX-3), and CHIRALPAK IA (IA) with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent].

Diethyl ether (Et_2O), toluene, dichloroethane ($(CH_2Cl)_2$), and dichloromethane (CH_2Cl_2) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Aminophosphonium chlorides **1**·HCl[1] and iminophosphoranes **1**[1] were prepared by following the literature procedure. Other simple chemicals were purchased and used as such.

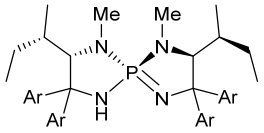
(1) D. Uraguchi, K. Yoshioka, Y. Ueki and T. Ooi, *J. Am. Chem. Soc.*, 2012, **134**, 19370.

Experimental Section:

Characterization of Catalysts:

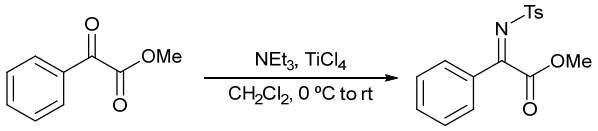


Tetraaminophosphonium Chloride 1e·HCl (Ar = 3-FC$_6$H$_4$): The synthesis was performed by following the literature procedure.[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (2H, d, $J_{P\text{-}H}$ = 15.0 Hz), 7.90 (2H, br), 7.45-7.36 (6H, m), 7.31 (2H, d, $J_{F\text{-}H}$ = 10.2 Hz), 7.07 (2H, br) 7.03 (2H, t, $J_{F\text{-}H}$ = 8.4 Hz, $J_{H\text{-}H}$ = 8.4 Hz), 6.94 (2H, t, $J_{F\text{-}H}$ = 8.4 Hz, $J_{H\text{-}H}$ = 8.4 Hz), 3.76 (2H, dd, $J_{P\text{-}H}$ = 21.0 Hz, $J_{H\text{-}H}$ = 4.8 Hz), 1.94-1.86 (2H, m), 1.89 (6H, d, $J_{P\text{-}H}$ = 10.2 Hz), 1.84-1.76 (2H, m), 0.97-0.86 (2H, m), 0.86 (6H, t, J = 7.2 Hz), 0.63 (6H, d, J = 6.6 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2 (d, $J_{F\text{-}C}$ = 248.7 Hz), 162.6 (d, $J_{F\text{-}C}$ = 245.7 Hz), 150.2 (d, $J_{F\text{-}C}$ = 5.9 Hz), 141.0 (d, $J_{F\text{-}C}$ = 7.2 Hz), 130.8 (d, $J_{F\text{-}C}$ = 8.8 Hz), 130.5 (d, $J_{F\text{-}C}$ = 8.8 Hz), 123.5, 122.5, 115.4 (d, $J_{F\text{-}C}$ = 23.1 Hz), 115.2 (d, $J_{F\text{-}C}$ = 5.7 Hz), 115.1 (d, $J_{F\text{-}C}$ = 7.2 Hz), 114.3 (d, $J_{F\text{-}C}$ = 24.6 Hz), 73.9 (d, $J_{P\text{-}C}$ = 11.5 Hz), 70.7 (d, $J_{P\text{-}C}$ = 10.1 Hz), 36.2, 32.4 (d, $J_{P\text{-}C}$ = 5.7 Hz), 25.2, 19.0, 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –100.9, –110.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.7; IR (film) 3055, 2967, 2716, 1612, 1589, 1489, 1437, 1339, 1238, 1186, 1022, 1001, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{44}N_4F_4P^+$ ([M–Cl]$^+$) 663.3234. Found 663.3211.; $[\alpha]_D^{24}$ –212.1 (c = 1.18, $CHCl_3$).



Triaminoiminophosphorane 1e (Ar = 3-FC$_6$H$_4$): The synthesis was performed by following the literature procedure.[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43-7.14 (12H, m), 6.94-6.82 (4H, m), 3.73 (2H, dd, $J_{P\text{-}H}$ = 18.6 Hz, $J_{H\text{-}H}$ = 2.7 Hz), 1.90 (2H, quin-dd, J = 7.2, 6.6, 2.7 Hz), 1.85 (6H, d, J = 9.0 Hz), 1.34 (2H, br), 0.92 (2H, d-quin, J = 16.8, 7.2 Hz), 0.75 (6H, d, J = 7.2 Hz), 0.68 (6H, t, J = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0 (d, $J_{F\text{-}C}$ = 244.3 Hz), 162.7 (d, $J_{F\text{-}C}$ = 245.8 Hz), 154.5, 147.4, 129.4 (d, $J_{F\text{-}C}$ = 7.2 Hz), 129.3 (d, $J_{F\text{-}C}$ = 7.2 Hz), 123.6, 122.3, 115.1 (d, $J_{F\text{-}C}$ = 23.1 Hz), 114.3 (d, $J_{F\text{-}C}$ = 21.7 Hz), 113.5, (d, $J_{F\text{-}C}$ = 18.9 Hz), 73.8, 71.1, 37.6, 32.3 (d, $J_{P\text{-}C}$ = 4.2 Hz), 24.7, 19.5, 12.4, one carbon atom was not found probably due to overlapping; ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.0; IR (film) 3451, 3405, 3067, 2965, 2876, 1611, 1587, 1485, 1439, 1327, 1230, 1194, 1136, 1107, 1001, 956 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{44}N_4F_4P^+$ ([M+H]$^+$) 663.3234. Found 663.3210.; $[\alpha]_D^{24}$ –251.4 (c = 1.00, $CHCl_3$).

Representative Procedure for Synthesis of *N*-Sulfonyl α-Imino Esters:

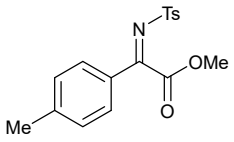


2a

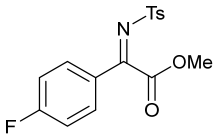
N-Sulfonyl α-imino esters were prepared by following the literature procedure with slight modification.[2] A solution of methyl benzoyl formate (1.28 g, 7.8 mmol), *p*-toluenesulfonamide (1.60 g, 9.4 mmol), and triethylamine (2.17 mL, 15.6 mmol) in CH_2Cl_2 (40 mL) was cooled to 0 °C. To the solution was added $TiCl_4$ (0.86 mL, 7.8 mmol) dropwise under Ar atmosphere. The solution was allowed to warm to ambient temperature and stirred until the complete consumption of methyl benzoyl formate. The reaction mixture was diluted with a mixed solvent of H/ethyl acetate (EA) (4:1, 10 mL) and filtered through a short plug of silica gel (H/EA = 4:1 as eluent). After removal of solvent under reduced pressure, the crude material was purified by silica gel column chromatography (H/EA = 20:1 → 4:1) and subsequent trituration with H/Et_2O

(2) J. S. Dickstein, M. W. Fennie, A. L. Norman, B. J. Paulose and M. C. Kozlowski, *J. Am. Chem. Soc*., 2008, **130**, 15794.(3) M. Hojo, M. Hojo, Y. Inoue and S. Tanimoto, *Bull. Chem. Soc. Jpn*., 1990, **63**, 2588.

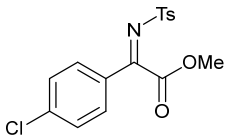
(10:1) afforded *N*-sulfonyl α-imino ester **2a** as a white solid (1.78 g, 5.6 mmol, 72%). **2a**[3]: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 7.5 Hz), 7.83 (2H, d, J = 7.5 Hz), 7.60 (1H, t, J = 7.5 Hz), 7.44 (2H, t, J = 7.5 Hz), 7.35 (2H, d, J = 7.5 Hz), 4.09 (3H, s), 2.44 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.4, 145.0, 135.6, 135.0, 131.4, 130.0, 129.9, 129.2, 128.3, 53.6, 21.8; IR (film) 3065, 2955, 1742, 1605, 1589, 1570, 1449, 1329, 1298, 1215, 1159, 1088, 1007 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}O_4NS^+$ ($[M+H]^+$) 318.0800. Found 318.0794.



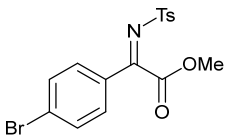
2b: colorless sticky oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.2 Hz), 7.72 (2H, d, J = 8.2 Hz), 7.34 (2H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.2 Hz), 4.08 (3H, s), 2.43 (3H, s), 2.41 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 165.6, 146.6, 144.8, 135.9, 130.2, 130.0, 129.9, 128.8, 128.2, 53.5, 22.0, 21.8; IR (film) 2955, 1744, 1587, 1557, 1435, 1323, 1304, 1221, 1159, 1088, 1009 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_4NNaS^+$ ($[M+Na]^+$) 354.0776. Found 354.0772.



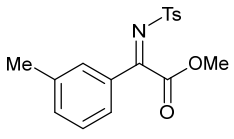
2c: colorless sticky oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.4 Hz), 7.86 (2H, dd, $J_{H\text{-}H}$ = 9.0 Hz, $J_{F\text{-}H}$ = 4.8 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.13 (2H, dd, $J_{F\text{-}H}$ = 9.0 Hz, $J_{H\text{-}H}$ = 9.0 Hz), 4.09 (3H, s), 2.44 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9 (d, $J_{F\text{-}C}$ = 258.8 Hz), 165.7, 165.2, 145.1, 135.5, 132.7 (d, $J_{F\text{-}C}$ = 10.1 Hz), 129.9, 128.3, 127.7 (d, $J_{F\text{-}C}$ = 2.9 Hz), 116.7 (d, $J_{F\text{-}C}$ = 23.3 Hz), 53.7, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –100.9; IR (film) 2957, 1742, 1595, 1574, 1508, 1449, 1327, 1306, 1215, 1155, 1088, 1008 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_4NFS^+$ ($[M+H]^+$) 336.0706. Found 336.0700.



2d: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.2 Hz), 7.77 (2H, dt, J = 9.2, 2.2 Hz), 7.42 (2H, dt, J = 9.2, 2.2 Hz), 7.35 (2H, d, J = 8.2 Hz), 4.09 (3H, s), 2.44 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.1, 145.2, 141.7, 135.4, 131.2, 130.0, 129.8, 129.6, 128.4, 53.8, 21.9; IR (film) 2955, 1742, 1607, 1584, 1557, 1435, 1404, 1331, 1306, 1215, 1161, 1088, 1005 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_4N^{35}ClS^+$ ($[M+H]^+$) 352.0410. Found 352.0406.

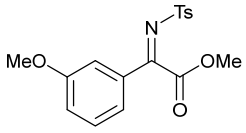


2e: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.2 Hz), 7.68 (2H, dt, J = 9.2, 2.1 Hz), 7.58 (2H, dt, J = 9.2, 2.1 Hz), 7.35 (2H, d, J = 8.2 Hz), 4.09 (3H, s), 2.44 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.0, 145.2, 135.3, 132.6, 131.2, 130.6, 130.3, 130.0, 128.3, 53.8, 21.8; IR (film) 2955, 1742, 1605, 1578, 1553, 1435, 1398, 1331, 1312, 1298, 1217, 1161, 1088, 1072, 1003 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_4N^{79}BrS^+$ ($[M+H]^+$) 395.9905. Found 395.9897.

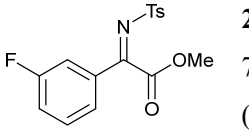


2f: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 8.4 Hz), 7.66 (1H, s), 7.61 (1H, d, J = 7.6 Hz), 7.41 (1H, d, J = 7.6 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.33 (1H, t, J = 7.6 Hz), 4.09 (3H, s), 2.44 (3H, s), 2.37 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 165.5, 145.0, 139.2, 135.9, 135.7, 131.3, 130.3, 129.9, 129.1, 128.3, 127.5, 53.6, 21.8, 21.4; IR (film) 2955, 1742, 1572, 1433, 1329, 1304, 1238, 1161, 1088, 1041 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}O_4NS^+$ ($[M+H]^+$) 332.0951. Found 332.0946.

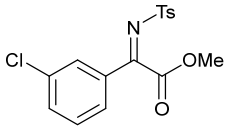
(3) M. Hojo, M. Hojo, Y. Inoue and S. Tanimoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2588.



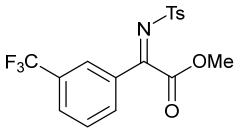
2g: orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 7.9 Hz), 7.40 (1H, t, J = 1.4 Hz), 7.38-7.31 (4H, m), 7.17-7.10 (1H, m), 4.08 (3H, s), 3.81 (3H, s), 2.44 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 165.4, 160.1, 145.1, 135.6, 132.7, 130.1, 129.9, 128.3, 123.2, 121.7, 113.6, 55.7, 53.6, 21.8; IR (film) 2955, 2837, 1742, 1605, 1570, 1487, 1450, 1431, 1327, 1250, 1202, 1159, 1088, 1016 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}O_5NS^+$ ([M+H]$^+$) 348.0906. Found 348.0897.



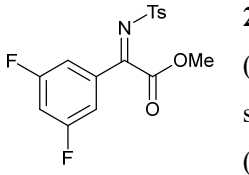
2h: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.2 Hz), 7.58 (1H, dd, J = 8.0, 2.3 Hz), 7.57 (1H, dd, J = 8.0, 1.5 Hz), 7.43 (1H, td, $J_{H\text{-}H}$ = 8.0 Hz, $J_{F\text{-}H}$ = 5.2 Hz), 7.36 (2H, d, J = 8.2 Hz), 7.30 (1H, dddd, $J_{F\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 8.0, 2.3, 1.5 Hz), 4.10 (3H, s), 2.45 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 164.9, 162.8 (d, $J_{F\text{-}C}$ = 250.1 Hz), 145.2, 135.3, 133.5 (d, $J_{F\text{-}C}$ = 7.3 Hz), 130.8 (d, $J_{F\text{-}C}$ = 7.3 Hz), 129.9, 128.3, 126.0, 122.0 (d, $J_{F\text{-}C}$ = 21.7 Hz), 116.2 (d, $J_{F\text{-}C}$ = 23.1 Hz), 53.7, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.5; IR (film) 3073, 2957, 1742, 1616, 1597, 1580, 1485, 1445, 1333, 1308, 1242, 1161, 1090, 1018, 953 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_4NFS^+$ ([M+H]$^+$) 336.0700. Found 336.0703.



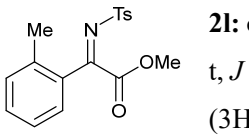
2i: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.4 Hz), 7.84 (1H, s), 7.67 (1H, d, J = 7.8 Hz), 7.56 (1H, d, J = 7.8 Hz), 7.40 (1H, t, J = 7.8 Hz), 7.36 (2H, d, J = 8.4 Hz), 4.10 (3H, s), 2.45 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 164.9, 145.3, 135.6, 135.3, 134.8, 133.1, 130.4, 130.0, 129.5, 128.4, 128.2, 53.8, 21.9; IR (film) 2955, 1744, 1607, 1562, 1427, 1333, 1302, 1211, 1161, 1090, 1018 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_4N^{35}ClS^+$ ([M+H]$^+$) 352.0410. Found 352.0409.



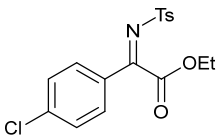
2j: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (1H, s), 7.98 (1H, d, J = 7.9 Hz), 7.94 (2H, d, J = 8.4 Hz), 7.85 (1H, d, J = 7.9 Hz), 7.60 (1H, t, J = 7.9 Hz), 7.37 (2H, d, J = 8.4 Hz), 4.11 (3H, s), 2.45 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 164.8, 145.5, 135.1, 133.1, 132.3, 132.0 (q, $J_{F\text{-}C}$ = 33.2 Hz), 131.1, 130.1, 129.9, 128.5, 126.4, 123.3 (q, $J_{F\text{-}C}$ = 274.9 Hz), 53.9, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 2957, 1744, 1595, 1435, 1333, 1285, 1209, 1163, 1130, 1090, 1018 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{15}O_4NF_3S^+$ ([M+H]$^+$) 386.0674. Found 386.0667.



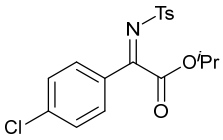
2k: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.4 Hz), 7.37 (2H, d, J = 8.4 Hz), 7.35 (2H, dd, $J_{F\text{-}H}$ = 7.8 Hz, $J_{H\text{-}H}$ = 1.8 Hz), 7.04 (1H, tt, $J_{F\text{-}H}$ = 7.8 Hz, $J_{H\text{-}H}$ = 1.8 Hz), 4.10 (3H, s), 2.46 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 164.4, 163.1 (dd, $J_{F\text{-}C}$ = 252.3, 12.2 Hz), 145.5, 135.0, 134.5 (t, $J_{F\text{-}C}$ = 8.5 Hz), 130.1, 128.5, 112.8 (dd, $J_{F\text{-}C}$ = 21.7, 5.8 Hz), 110.1 (t, $J_{F\text{-}C}$ = 25.3 Hz), 54.0, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –107.0; IR (film) 3086, 2957, 1742, 1624, 1589, 1437, 1335, 1269, 1163, 1126, 1090, 993 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_4NF_2S^+$ ([M+H]$^+$) 354.0612. Found 354.0604.



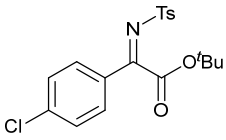
2l: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.4 Hz), 7.52 (1H, d, J = 7.8 Hz), 7.41 (1H, t, J = 7.8 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.26 (1H, t, J = 7.8 Hz), 7.25 (1H, d, J = 7.8 Hz), 4.05 (3H, s), 2.45 (3H, s), 2.44 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 165.4, 144.9, 141.1, 136.1, 133.2, 132.8, 131.4, 130.5, 129.9, 129.7, 128.2, 126.4, 53.6, 22.3, 21.8; IR (film) 2955, 1742, 1597, 1562, 1456, 1329, 1308, 1211, 1159, 1088, 1005 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_4NNaS^+$ ([M+Na]$^+$) 354.0776. Found 354.0765.



2m: colorless sticky oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.4 Hz), 7.78 (2H, d, J = 8.4 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.35 (2H, d, J = 8.4 Hz), 4.57 (2H, q, J = 7.2 Hz), 2.44 (3H, s), 1.48 (3H, t, J = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 164.6, 145.1, 141.6, 135.6, 131.2, 130.0, 129.9, 129.6, 128.3, 63.5, 21.8, 14.1; IR (film) 2984, 1740, 1609, 1584, 1558, 1404, 1333, 1298, 1211, 1163, 1088, 1011 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_4N^{35}ClS^+$ ([M+H]$^+$) 366.0567. Found 366.0560.

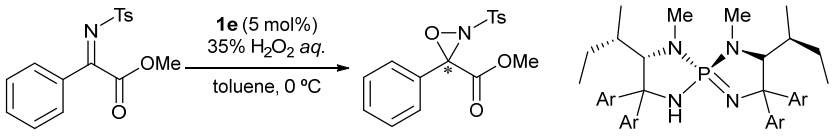


2n: colorless sticky oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.4 Hz), 7.78 (2H, d, J = 8.4 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.35 (2H, d, J = 8.4 Hz), 5.47 (1H, septet, J = 6.2 Hz), 2.44 (3H, s), 1.48 (6H, d, J = 6.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 164.1, 145.0, 141.5, 135.7, 131.2, 130.2, 129.9, 129.6, 128.3, 72.1, 21.8, one carbon atom was not found probably due to overlapping; IR (film) 2984, 1734, 1609, 1584, 1557, 1489, 1404, 1331, 1294, 1215, 1161, 1088, 997 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{19}O_4N^{35}ClS^+$ ([M+H]$^+$) 380.0723. Found 380.0713.



2o: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 8.1 Hz), 7.80 (2H, d, J = 8.7 Hz), 7.41 (2H, d, J = 8.7 Hz), 7.34 (2H, d, J = 8.1 Hz), 2.44 (3H, s), 1.70 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 163.3, 144.9, 141.2, 135.9, 131.2, 130.6, 129.9, 129.5, 128.3, 86.7, 28.2, 21.8; IR (film) 2982, 1734, 1607, 1584, 1558, 1456, 1404, 1371, 1333, 1227, 1161, 1090, 995 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}O_4N^{35}ClS^+$ ([M+H]$^+$) 394.0880. Found 394.0875.

Representative Procedure for the Catalytic Asymmetric Oxidation of *N*-Sulfonyl α-Imino Esters:

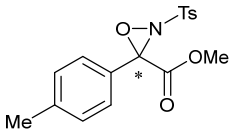


2a **3a** **1e** (Ar = 3-FC_6H_4)

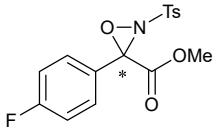
To a solution of α-imino ester **2a** (63.5 mg, 0.2 mmol) and iminophosphorane **1e** (6.81 mg, 0.01 mmol) in toluene (4.0 mL) was added a 35% aqueous solution of hydrogen peroxide (34.4 μL, 0.4 mmol) dropwise and the reaction mixture was stirred for 12 h at 0 ºC under Ar atmosphere. The resulting solution was diluted with a saturated aqueous solution of Na_2SO_3 and extracted with EA twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. All volatiles were removed under reduced pressure and the crude residue thus obtained was purified by column chromatography on silica gel (H/EA = 20:1 → 10:1 → 4:1) to afford oxaziridine **3a** as a white solid (54.7 mg, 0.16 mmol, 82%). The enantiomeric excess of **3a** was determined to be 97% ee by HPLC analysis. **3a**[4]: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.4 Hz), 7.51 (2H, d, J = 7.2 Hz), 7.45 (1H, t, J = 7.2 Hz), 7.41 (2H, d, J = 8.4 Hz), 7.39 (2H, t, J = 7.2 Hz), 4.02 (3H, s), 2.48 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 146.7, 132.7, 131.4, 130.4, 130.2, 129.6, 128.9, 127.4, 84.3, 53.7, 22.0; IR (film) 2955, 1751, 1595, 1454, 1437, 1358, 1277, 1202, 1171, 1088, 1005 cm^{-1}; HRMS (ESI)

(4) The ^{1}H NMR analysis showed that oxaziridine **3** existed as a mixture of diastereomers with respect to the "stereogenic" nitrogen atom (dr = 10:1 to 7:1), but the diastereomers were supposed to be under equilibrium at room temperature.

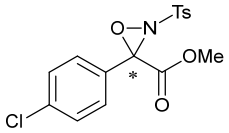
Calcd for $C_{16}H_{15}O_5NNaS^+$ ([M+Na]$^+$) 356.0569. Found 356.0562.; $[\alpha]_D^{26}$ +77.0 (c = 4.13, $CHCl_3$) for 97% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 16.9 min (minor enantiomer), 28.3 min (major enantiomer).



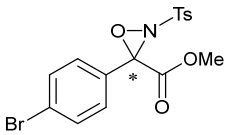
3b: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.4 Hz), 7.38 (2H, d, J = 8.4 Hz), 7.19 (2H, d, J = 8.4 Hz), 4.01 (3H s), 2.48 (3H, s), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 146.7, 141.8, 132.8, 130.2, 129.6, 127.4, 84.4, 53.6, 22.0, 21.5, two carbon atoms were not found probably due to overlapping; IR (film) 2955, 1749, 1684, 1603, 1437, 1358, 1279, 1204, 1171, 1088, 1007 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_5NNaS^+$ ([M+Na$^+$]) 370.0725. Found 370.0713.; $[\alpha]_D^{26}$ +55.0 (c = 1.87, $CHCl_3$) for 98% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 21.5 min (minor enantiomer), 27.9 min (major enantiomer).



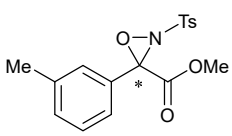
3c: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.4 Hz), 7.50 (2H, dd, $J_{H\text{-}H}$ = 8.4 Hz, $J_{F\text{-}H}$ = 4.8 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.08 (2H, dd, $J_{H\text{-}H}$ = 8.4 Hz, $J_{F\text{-}H}$ = 8.4 Hz), 4.02 (3H, s), 2.49 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6 (d, $J_{F\text{-}C}$ = 253.1 Hz), 163.9, 146.9, 132.5, 130.2, 129.7 (d, $J_{F\text{-}C}$ = 8.6 Hz), 129.6, 126.3 (d, $J_{F\text{-}C}$ = 4.2 Hz), 116.1 (d, $J_{F\text{-}C}$ = 23.1 Hz), 83.7, 53.8, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –100.9; IR (film) 2959, 1755, 1597, 1510, 1439, 1360, 1281, 1238, 1204, 1173, 1157, 1090, 1007 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_5NFNaS^+$ ([M+Na]$^+$) 374.0469. Found 374.0463.; $[\alpha]_D^{23}$ +58.5 (c = 1.35, $CHCl_3$) for 95% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 230 nm, 7.9 min (major enantiomer), 8.9 min (minor enantiomer).



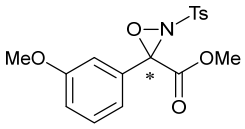
3d: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.0 Hz), 7.44 (2H, d, J = 8.8 Hz), 7.42 (2H, d, J = 8.0 Hz), 7.37 (2H, d, J = 8.8 Hz), 4.02 (3H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 146.9, 137.8, 132.5, 130.2, 129.6, 129.2, 129.0, 128.9, 83.6, 53.9, 22.0; IR (film) 2957, 1755, 1595, 1493, 1439, 1408, 1360, 1275, 1204, 1173, 1090, 1005 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_5N^{35}ClNaS^+$ ([M+Na]$^+$) 390.0179. Found 390.0169.; $[\alpha]_D^{24}$ +48.0 (c = 1.69, $CHCl_3$) for 96% ee; HPLC OD-3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 230 nm, 10.0 min (major enantiomer), 11.7 min (minor enantiomer).



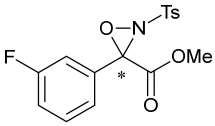
3e: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.0 Hz), 7.53 (2H, J = 8.4 Hz), 7.42 (2H, d, J = 8.0 Hz), 7.37 (2H, d, J = 8.4 Hz), 4.02 (3H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 146.9, 132.4, 132.2, 130.2, 129.6, 129.5, 129.0, 126.1, 83.7, 53.9, 22.0; IR (film) 2957, 1751, 1593, 1489, 1437, 1402, 1358, 1279, 1202, 1171, 1088, 1003 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_5N^{79}BrNaS^+$ ([M+Na]$^+$) 433.9674. Found 433.9669.; $[\alpha]_D^{24}$ +48.1 (c = 1.75, $CHCl_3$) for 97% ee; HPLC OD-3, H/IPA = 49:1, flow rate = 1.0 mL/min, λ = 230 nm, 16.7 min (major enantiomer), 19.6 min (minor enantiomer).



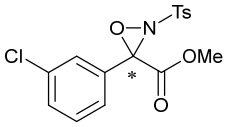
3f: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.0 Hz), 7.41 (2H, d, J = 8.0 Hz), 7.33-7.24 (4H, m), 4.01 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 146.7, 138.9, 132.7, 132.1, 130.2$_2$, 130.1$_8$, 129.6, 128.8, 127.7, 124.5, 84.4, 53.7, 22.0, 21.5; IR (film) 2955, 1761, 1595, 1437, 1358, 1333, 1288, 1219, 1171, 1090, 1038 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_5NNaS^+$ ([M+Na]$^+$) 370.0720. Found 370.0722.; $[\alpha]_D^{26}$ +69.8 (c = 0.82, $CHCl_3$) for 96% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 15.1 min (minor enantiomer), 27.1 min (major enantiomer).



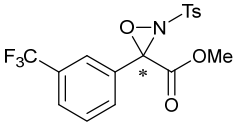
3g: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.2 Hz), 7.40 (2H, d, J = 8.2 Hz), 7.29 (1H, t, J = 7.6 Hz), 7.11 (1H, d, J = 7.6 Hz), 7.01 (1H, t, J = 2.3 Hz), 6.97 (1H, dd, J = 7.6, 2.3 Hz), 4.00 (3H, s), 3.78 (3H, s), 2.48 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 160.0, 146.8, 132.7, 131.7, 130.2, 130.0, 129.6, 119.7, 117.4, 112.4, 84.2, 55.6, 53.7, 22.0; IR (film) 2957, 1755, 1597, 1489, 1433, 1358, 1290, 1233, 1169, 1088, 1043, 1015 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_6NNaS^+$ ([M+Na]$^+$) 386.0674. Found 386.0668.; $[\alpha]_D^{25}$ +71.6 (c = 1.72, $CHCl_3$) for 97% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 230 nm, 9.5 min (major enantiomer), 12.6 min (minor enantiomer).



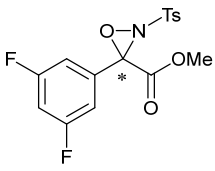
3h: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (2H, d, J = 8.4 Hz), 7.43 (2H, d, J = 8.4 Hz), 7.37 (1H, td, $J_{H\text{-}H}$ = 8.0 Hz, $J_{F\text{-}H}$ = 5.6 Hz), 7.32 (1H, dt, J = 8.0, 1.4 Hz), 7.21 (1H, ddd, $J_{F\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 2.2, 1.4 Hz), 7.15 (1H, dddd, $J_{F\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 8.0, 2.2, 1.4 Hz), 4.03 (3H, s), 2.49 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 161.5 (d, $J_{F\text{-}C}$ = 249.7 Hz), 146.9, 132.7 (d, $J_{F\text{-}C}$ = 7.8 Hz), 132.4, 130.6 (d, $J_{F\text{-}C}$ = 7.8 Hz), 130.2, 129.6, 123.1 (d, $J_{F\text{-}C}$ = 2.9 Hz), 118.5 (d, $J_{F\text{-}C}$ = 21.3 Hz), 114.6 (d, $J_{F\text{-}C}$ = 24.2 Hz), 83.3, 53.8, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –110.9; IR (film) 2957, 1763, 1593, 1360, 1335, 1288, 1221, 1171, 1088, 1018 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_5NFNaS^+$ ([M+Na]$^+$) 374.0474. Found 374.0466.; $[\alpha]_D^{24}$ +73.8 (c = 0.84, $CHCl_3$) for 95% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 230 nm, 7.6 min (major enantiomer), 10.1 min (minor enantiomer).



3i: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.4 Hz), 7.49 (1H, t, J = 1.8 Hz), 7.44-7.39 (4H, m), 7.33 (1H, t, J = 8.0 Hz), 4.02 (3H, s), 2.49 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 147.0, 135.1, 132.3$_8$, 132.3$_6$, 131.6, 130.3, 130.2, 129.6, 127.5, 125.6, 83.4, 53.9, 22.0; IR (film) 2955, 1755, 1595, 1427, 1360, 1331, 1287, 1204, 1173, 1088, 1018 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O_5N^{35}ClNaS^+$ ([M+Na]$^+$) 390.0179. Found 390.0174.; $[\alpha]_D^{27}$ +65.5 (c = 1.29, $CHCl_3$) for 95% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.5 min (minor enantiomer), 22.7 min (major enantiomer).

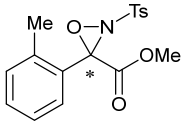


3j: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.2 Hz), 7.74 (1H, s), 7.73 (1H, d, J = 7.8 Hz), 7.72 (1H, d, J = 7.8 Hz), 7.54 (1H, t, J = 7.8 Hz), 7.43 (2H, d, J = 8.2 Hz), 4.04 (3H, s), 2.49 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 147.1, 132.3, 131.7, 131.6 (q, $J_{F\text{-}C}$ = 33.2 Hz), 130.9, 130.3, 129.6$_4$, 129.5$_7$, 128.2 (q, $J_{F\text{-}C}$ = 2.9 Hz), 124.3 (q, $J_{F\text{-}C}$ = 4.3 Hz), 123.5 (q, $J_{F\text{-}C}$ = 271.8 Hz), 83.3, 54.0, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8; IR (film) 2957, 1757, 1595, 1437, 1362, 1333, 1263, 1171, 1130, 1018 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{14}O_5NF_3NaS^+$ ([M+Na]$^+$) 424.0442. Found 424.0432.; $[\alpha]_D^{24}$ +52.5 (c = 0.82, $CHCl_3$) for 85% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 7.5 min (minor enantiomer), 14.5 min (major enantiomer).

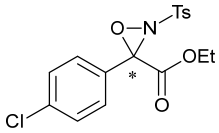


3k: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (2H, d, J = 8.2 Hz), 7.43 (2H, d, J = 8.2 Hz), 7.07 (2H, dt, $J_{F\text{-}H}$ = 7.8 Hz, $J_{H\text{-}H}$ = 2.2 Hz), 6.91 (1H, tt, $J_{F\text{-}H}$ = 8.4 Hz, $J_{H\text{-}H}$ = 2.2 Hz), 4.04 (3H, s), 2.49 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3, 163.1 (dd, $J_{F\text{-}C}$ = 250.9, 12.3 Hz), 147.1, 134.1 (t, $J_{F\text{-}C}$ = 8.8 Hz), 132.2, 130.3, 129.6, 110.9 (dd, $J_{F\text{-}C}$ = 22.5, 6.5 Hz), 107.0 (t, $J_{F\text{-}C}$ = 25.3 Hz), 82.8, 54.1, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ –107.0; IR (film) 2959, 1755, 1601, 1437, 1362, 1339, 1244, 1173, 1126, 1090, 993 cm^{-1}; HRMS

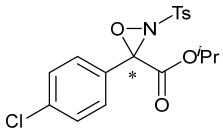
(ESI) Calcd for $C_{16}H_{13}O_5NF_2NaS^+$ ([M+Na]$^+$) 392.0380. Found 392.0376.; $[\alpha]_D^{24}$ +50.8 (c = 1.05, $CHCl_3$) for 82% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 7.8 min (minor enantiomer), 14.3 min (major enantiomer).



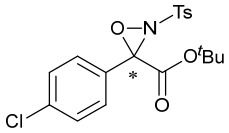
3l: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.0 Hz), 7.44 (1H, d, J = 8.0 Hz), 7.39 (2H, d, J = 8.0 Hz), 7.30 (1H, t, J = 8.0 Hz), 7.20 (1H, t, J = 8.0 Hz), 7.17 (1H, d, J = 8.0 Hz), 3.90 (3H, s), 2.51 (3H, s), 2.46 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 146.8, 136.9, 132.7, 131.0, 130.3, 130.2, 129.6, 129.2, 127.8, 126.0, 85.7, 53.7, 21.9, 19.0; IR (film) 2955, 1759, 1595, 1456, 1437, 1360, 1271, 1173, 1090, 1003, 916 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_5NNaS^+$ ([M+Na]$^+$) 370.0725. Found 370.0719.; $[\alpha]_D^{25}$ +70.1 (c = 1.05, $CHCl_3$) for 99% ee; HPLC AY-3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 230 nm, 9.7 min (minor enantiomer), 13.2 min (major enantiomer).



3m: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 7.8 Hz), 7.41 (2H, d, J = 8.4 Hz), 7.36 (2H, d, J = 7.8 Hz), 4.51 (1H, dq, J = 10.8, 7.2 Hz), 4.46 (1H, dq, J = 10.8, 7.2 Hz), 2.48 (3H, s), 1.44 (3H, t, J = 7.2 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3, 146.8, 137.7, 132.6, 130.2, 129.6, 129.1$_9$, 129.1$_6$, 128.9, 83.7, 63.5, 22.0, 14.0; IR (film) 2986, 1759, 1597, 1493, 1360, 1275, 1192, 1171, 1090, 1015 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{16}O_5N^{35}ClNaS^+$ ([M+Na]$^+$) 404.0335. Found 404.0327.; $[\alpha]_D^{24}$ +54.5 (c = 1.20, $CHCl_3$) for 95% ee; HPLC OD-3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 230 nm, 8.0 min (major enantiomer), 8.8 min (minor enantiomer).

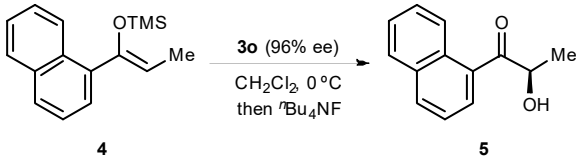


3n: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 7.8 Hz), 7.41 (2H, d, J = 8.4 Hz), 7.36 (2H, d, J = 7.8 Hz), 5.35 (1H, septet, J = 6.3 Hz), 2.48 (3H, s), 1.43 (3H, d, J = 6.3 Hz), 1.42 (3H, d, J = 6.3 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 146.7, 137.6, 132.8, 130.2, 129.5, 129.4, 129.2, 128.9, 83.6, 72.0, 22.0, 21.7, 21.6; IR (film) 2984, 2934, 1755, 1597, 1493, 1360, 1279, 1194, 1169, 1090, 991 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}O_5N^{35}ClNaS^+$ ([M+Na]$^+$) 418.0492. Found 418.0489.; $[\alpha]_D^{24}$ +55.6 (c = 0.94, $CHCl_3$) for 95% ee; HPLC OD-3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 230 nm, 6.6 min (major enantiomer), 7.3 min (minor enantiomer).



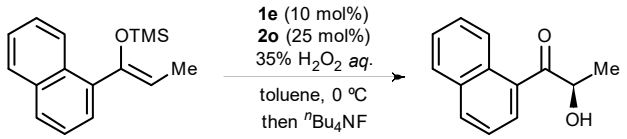
3o: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.4 Hz), 7.46 (2H, d, J = 7.8 Hz), 7.40 (2H, d, J = 8.4 Hz), 7.36 (2H, d, J = 7.8 Hz), 2.48 (3H, s), 1.63 (9H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 146.6, 137.4, 133.1, 130.2, 129.9, 129.5, 129.1, 128.9, 86.2, 83.7, 28.0, 22.0; IR (film) 2982, 1749, 1597, 1493, 1360, 1283, 1202, 1169, 1150, 1090, 988, 912 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{20}O_5N^{35}ClNaS^+$ ([M+Na]$^+$) 432.0648. Found 432.0645.; $[\alpha]_D^{26}$ +64.2 (c = 1.04, $CHCl_3$) for 96% ee; HPLC OD-3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 230 nm, 5.9 min (major enantiomer), 6.6 min (minor enantiomer).

Representative Procedure for Asymmetric Rubottom Oxidation of Silyl Enol Ether:



Oxaziridine **3o** (60.6 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (1.2 mL) and the solution was cooled to 0 ºC. Silyl enol ether **4**[5] (30.8 mg, 0.12 mmol) was added to the solution slowly and the reaction mixture was stirred for 12 h at 0 ºC. The reaction was quenched by addition of dimethyl sulfide (20.0 μL) and the stirring was continued for 1 h. Then, a 1.0 M solution of TBAF in THF (150 μL, 0.15 mmol) was added and the resulting mixture was further stirred for 30 min at 0 ºC. The resulting solution was diluted with H_2O and extracted with EA twice. The combined organic extracts were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel (H/EA = 20:1 → 10:1 → 4:1) to afford α-hydroxy ketone **5** as a colorless oil (22.1 mg, 0.11 mmol, 90%). The enantiomeric excess of **5** was determined to be 92% ee by HPLC analysis. **5**[6]**:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (1H, d, J = 7.8 Hz), 8.05 (1H, d, J = 7.8 Hz), 7.91 (1H, d, J = 7.8 Hz), 7.79 (1H, d, J = 7.8 Hz), 7.63 (1H, dt, J = 7.8, 1.4 Hz), 7.58 (1H, t, J = 7.8 Hz), 7.53 (1H, t, J = 7.8 Hz), 5.24 (1H, dq, J = 7.2, 5.4 Hz), 3.94 (1H, d, J = 5.4 Hz), 1.36 (3H, d, J = 7.2 Hz); $[\alpha]_D^{27}$ +150.3 (c = 1.68, $CHCl_3$) for 92% ee; HPLC OD-3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 9.0 min (minor enantiomer), 9.8 min (major enantiomer).

Representative Procedure for Dual Catalytic Asymmetric Rubottom Oxidation of Silyl Enol Ether:



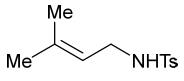
4 **5**

Silyl enol ether **4** (25.6 mg, 0.1 mmol), iminophosphorane **1e** (6.81 mg, 0.01 mmol), and α-imino ester **2o** (9.85 mg, 0.025 mmol) were dissolved into toluene (200 μL) at 0 ºC. A 35% aqueous solution of hydrogen peroxide (17.2 μL, 0.2 mmol) was added to the solution dropwise and the reaction mixture was stirred for 72 h at 0 ºC. The reaction was quenched by addition of dimethyl sulfide (20.0 μL). After 30 min of stirring, a saturated aqueous solution of Na_2SO_3 was added to the solution and the whole mixture was extracted with EA three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, and filtered. All volatiles were removed by evaporation and the residue was dissolved into CH_2Cl_2 (1.0 mL). To the solution was added a 1 M solution of TBAF in THF (120 μL, 0.12 mmol) and the mixture was stirred for 30 min at 0 ºC. The resulting solution was diluted with H_2O and extracted with EA twice. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the crude material thus obtained was purified by column chromatography on silica gel (H/EA = 20:1 → 10:1 → 4:1) to afford the product **5** as a colorless oil (18.2 mg, 0.091 mmol, 91%). The enantiomeric excess of the product was determined to be 92% ee by HPLC analysis.

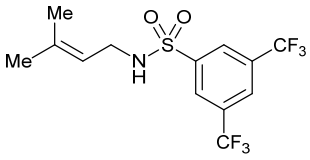
Preparation of Allylic Sulfonamides:

Allylic and homoallylic sulfonamides **8** were prepared from the corresponding allylic or homoallylic bromides and aryl sulfonamide according to the literature procedure.[7]

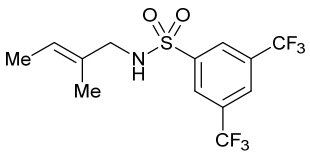
(5) S. E. Denmark, S. Rossi, M. P. Webster and H. Wang, *J. Am. Chem. Soc*., 2014, **136**, 13016.
(6) R. J. Lukas, A. Z. Muresan, M. I. Damaj, B. E. Blough, X. Huang, H. A. Navarro, W. Mascarella, J. B. Eaton, S. K. Marxer-Miller and F. I. Carroll, *J. Med. Chem.*, 2010, **53**, 4731.
(7) W. Wang, J. Yang, F. Wang and M. Shi, *Organometallics*, 2011, **30**, 3859.



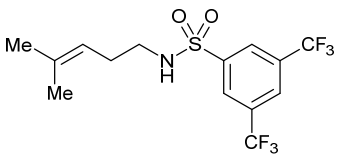
8a[8]**:** white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (2H, d, J = 8.0 Hz), 7.31 (2H, d, J = 8.0 Hz), 5.06 (1H, t, J = 6.4 Hz), 4.17 (1H, br), 3.54 (2H, t, J = 6.4 Hz), 2.43 (3H, s), 1.64 (3H, s), 1.54 (3H,s).



8b: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (2H, s), 8.07 (1H, s), 5.00 (1H, t, J = 6.6 Hz), 4.57 (1H, br), 3.69 (2H, t, J = 6.6 Hz), 1.62 (3H, s), 1.58 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 138.9, 133.0 (q, $J_{F\text{-}C}$ = 34.6 Hz), 127.5, 126.2, 122.6 (q, $J_{F\text{-}C}$ = 273.3 Hz), 118.4, 41.4, 25.6, 17.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 3285, 2980, 1423, 1361, 1341, 1281, 1159, 1136, 1040, 903 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{12}O_2NF_6S^-$ ([M–H]$^-$) 360.0493. Found 360.0490.

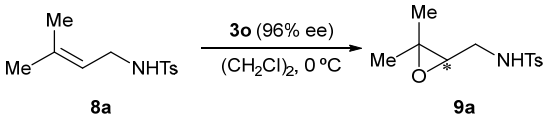


8c: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (2H, s), 8.06 (1H, s), 5.39 (1H, q, J = 6.6 Hz), 4.79 (1H, br), 3.60 (2H, d, J = 6.0 Hz), 1.50 (3H, d, J = 6.6 Hz), 1.49 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 132.9 (q, $J_{F\text{-}C}$ = 34.7 Hz), 130.1, 127.5, 126.2 (q, $J_{F\text{-}C}$ = 3.6 Hz), 124.6, 122.6 (q, $J_{F\text{-}C}$ = 273.2 Hz), 51.5, 13.8, 13.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 3296, 3088, 2934, 2864, 1418, 1362, 1275, 1165, 1130, 1113, 1051, 905 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{12}O_2NF_6S^-$ ([M–H]$^-$) 360.0493. Found 360.0489.



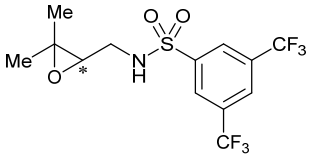
8d: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (2H, s), 8.07 (1H, s), 4.93 (1H, t, J = 6.9 Hz), 4.56 (1H, br), 3.06 (2H, q, J = 6.9 Hz), 2.20 (2H, q, J = 6.9 Hz), 1.68 (3H, s), 1.58 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 136.6, 133.1 (q, $J_{F\text{-}C}$ = 33.2 Hz), 127.4, 126.2, 122.5 (q, $J_{F\text{-}C}$ = 273.3 Hz), 119.1, 43.2, 28.3, 25.8, 17.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 3287, 2986, 1626, 1427, 1360, 1281, 1161, 1136, 1069, 902 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{14}O_2NF_6S^-$ ([M–H]$^-$) 374.0649. Found 374.0645.

Representative Procedure for Asymmetric Epoxidation of Allylic Sulfonamides:

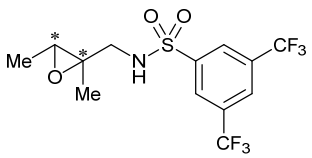


To a solution of allylic sulfonamide **8a** (24.0 mg, 0.1 mmol) in $(CH_2Cl)_2$ (300 μL) was added oxaziridine **3o** (48.8 mg, 0.12 mmol) at 0 ºC. After being stirred for 72 h, the reaction mixture was quenched by addition of dimethyl sulfide (20.0 μL) and was further stirred for 30 min at 0 ºC. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography on silica gel (pure CH_2Cl_2 then H/EA = 4:1 → 2:1) to afford **9a** as a white solid (20.9 mg, 0.082 mmol, 82%). The enantiomeric excess of **9a** was determined to be 88% ee by HPLC analysis. **9a**[9]**:** white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (2H, d, J = 8.4 Hz), 7.32 (2H, d, J = 8.4 Hz), 4.70 (1H, br), 3.28 (1H, ddd, J = 13.6, 8.1, 5.0 Hz), 2.97 (1H, ddd, J = 13.6, 6.6, 5.0 Hz), 2.84 (1H, dd, J = 6.6, 5.0 Hz), 2.43 (3H, s), 1.26 (3H, s), 1.21 (3H, s); $[\alpha]_D^{27}$ +37.0 (c = 1.52, $CHCl_3$) for 88% ee; HPLC IA, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 26.3 min, (minor enantiomer), 37.5 min (major enantiomer).

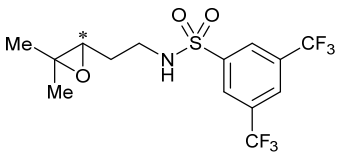
(8) K.-B. Wang, R.-Q. Ran, S.-D. Xiu and C.-Y. Li, *Org. Lett*., 2013, **15**, 2374.
(9) J. L. Olivares-Romero, Z. Li and H. Yamamoto, *J. Am. Chem. Soc*., 2012, **134**, 5440.



9b: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (2H, s), 8.09 (1H, s), 5.06 (1H, br), 3.46 (1H, ddd, J = 13.6, 8.0, 4.4 Hz), 3.03 (1H, ddd, J = 13.6, 8.0, 4.4 Hz), 2.88 (1H, dd, J = 8.0, 4.4 Hz), 1.30 (3H, s), 1.26 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 133.2 (q, $J_{F\text{-}C}$ = 34.7 Hz), 127.5, 126.5, 122.6 (q, $J_{F\text{-}C}$ = 273.2 Hz), 61.8, 59.7, 43.2, 24.5, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 3262, 3084, 1447, 1354, 1288, 1165, 1134, 1070, 903 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{13}O_3NF_6NaS^+$ ([M+Na]$^+$) 400.0418. Found 400.0409.; $[\alpha]_D^{27}$ +34.5 (c = 1.14, $CHCl_3$) for 92% ee; HPLC OX-3, H/IPA = 49:1, flow rate = 0.5 mL/min, λ = 210 nm, 28.7 min (major enantiomer), 32.7 min (minor enantiomer).

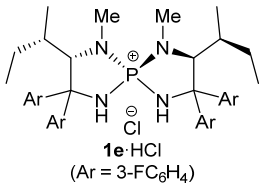


9c: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (2H, s), 8.08 (1H, s), 5.08 (1H, br), 3.22 (1H, dd, J = 13.2, 5.1 Hz), 3.15 (1H, dd, J = 13.2, 7.5 Hz), 3.08 (1H, q, J = 5.4 Hz), 1.30 (3H, d, J = 5.4 Hz), 1.29 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 133.1 (q, $J_{F\text{-}C}$ = 34.7 Hz), 127.4, 126.4 (q, $J_{F\text{-}C}$ = 2.9 Hz), 122.6 (q, $J_{F\text{-}C}$ = 274.8 Hz), 59.4, 56.9, 48.5, 15.0, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 3237, 3088, 1626, 1423, 1354, 1285, 1165, 1132, 905 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{13}O_3NF_6NaS^+$ ([M+Na]$^+$) 400.0418. Found 400.0417.; $[\alpha]_D^{25}$ –9.3 (c = 2.42, $CHCl_3$) for 87% ee; HPLC OX-3, H/IPA = 19:1, flow rate = 0.5 mL/min, λ = 210 nm, 12.3 min (minor enantiomer), 13.5 min (major enantiomer).

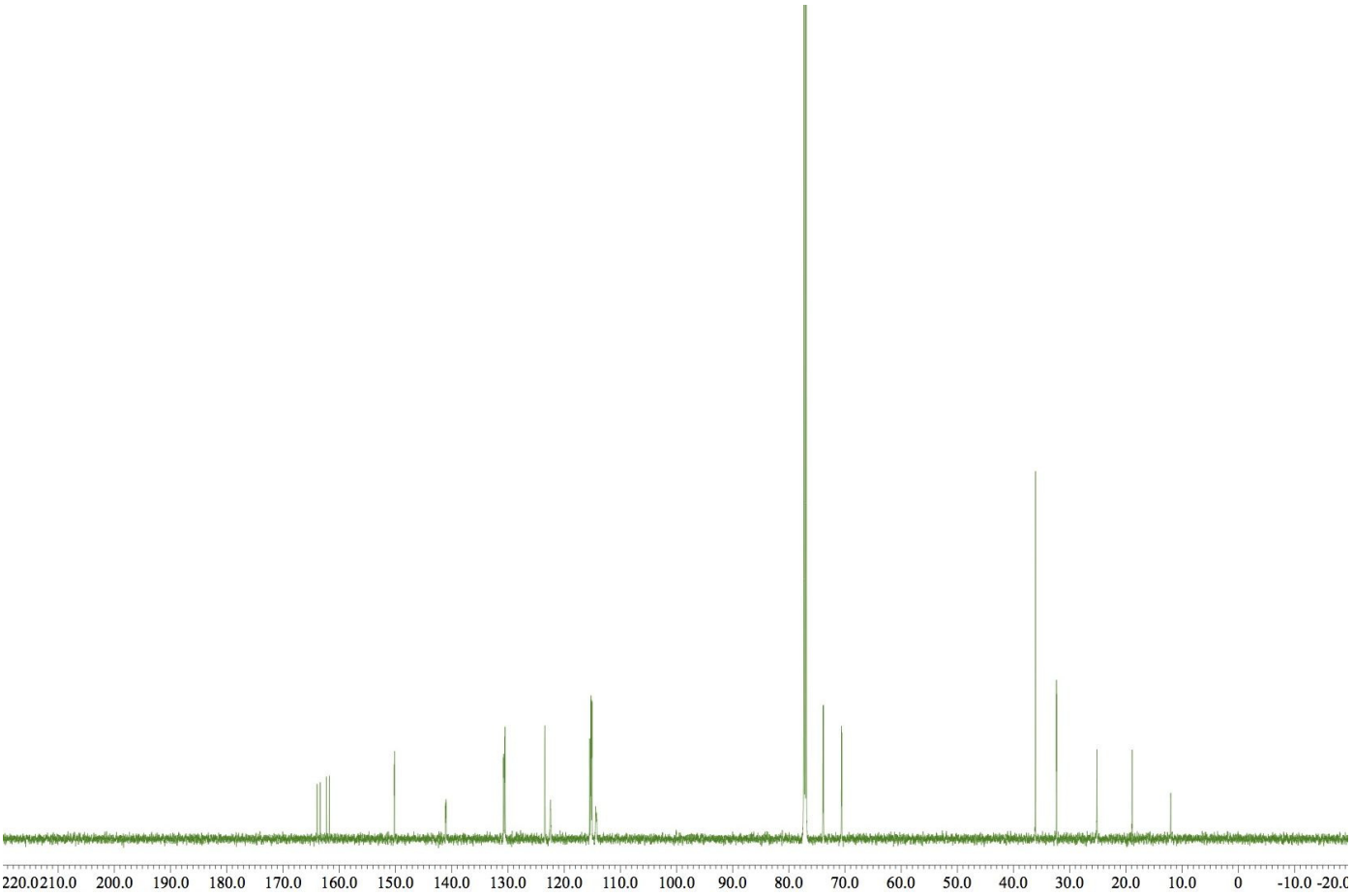


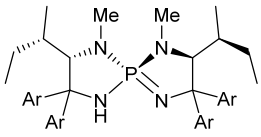
9d: white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (2H, s), 8.07 (1H, s), 5.44 (1H, br), 3.32 (1H, dq, J = 12.6, 5.4 Hz), 3.19 (1H, ddt, J = 12.6, 9.0, 5.4 Hz), 2.73 (1H, dd, J = 9.0, 5.4 Hz), 1.96 (1H, dq, J = 14.1, 5.4 Hz), 1.56 (1H, dtd, J = 14.1, 9.0, 5.4 Hz), 1.29 (3H, s), 1.24 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 133.1 (q, $J_{F\text{-}C}$ = 33.8 Hz), 127.5, 126.3 (q, $J_{F\text{-}C}$ = 2.9 Hz), 122.6 (q, $J_{F\text{-}C}$ = 274.8 Hz), 62.4, 58.7, 41.8, 28.4, 24.6, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; IR (film) 3289, 2974, 2930, 1626, 1435, 1360, 1279, 1161, 1136, 1113, 905 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{15}O_3NF_6NaS^+$ ([M+Na]$^+$) 414.0575. Found 414.0558.; $[\alpha]_D^{25}$ +16.7 (c = 2.75, $CHCl_3$) for 90% ee; HPLC AY-3, H/IPA = 19:1, flow rate = 1.0 mL/min, λ = 210 nm, 14.0 min (minor enantiomer), 18.1 min (major enantiomer).

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

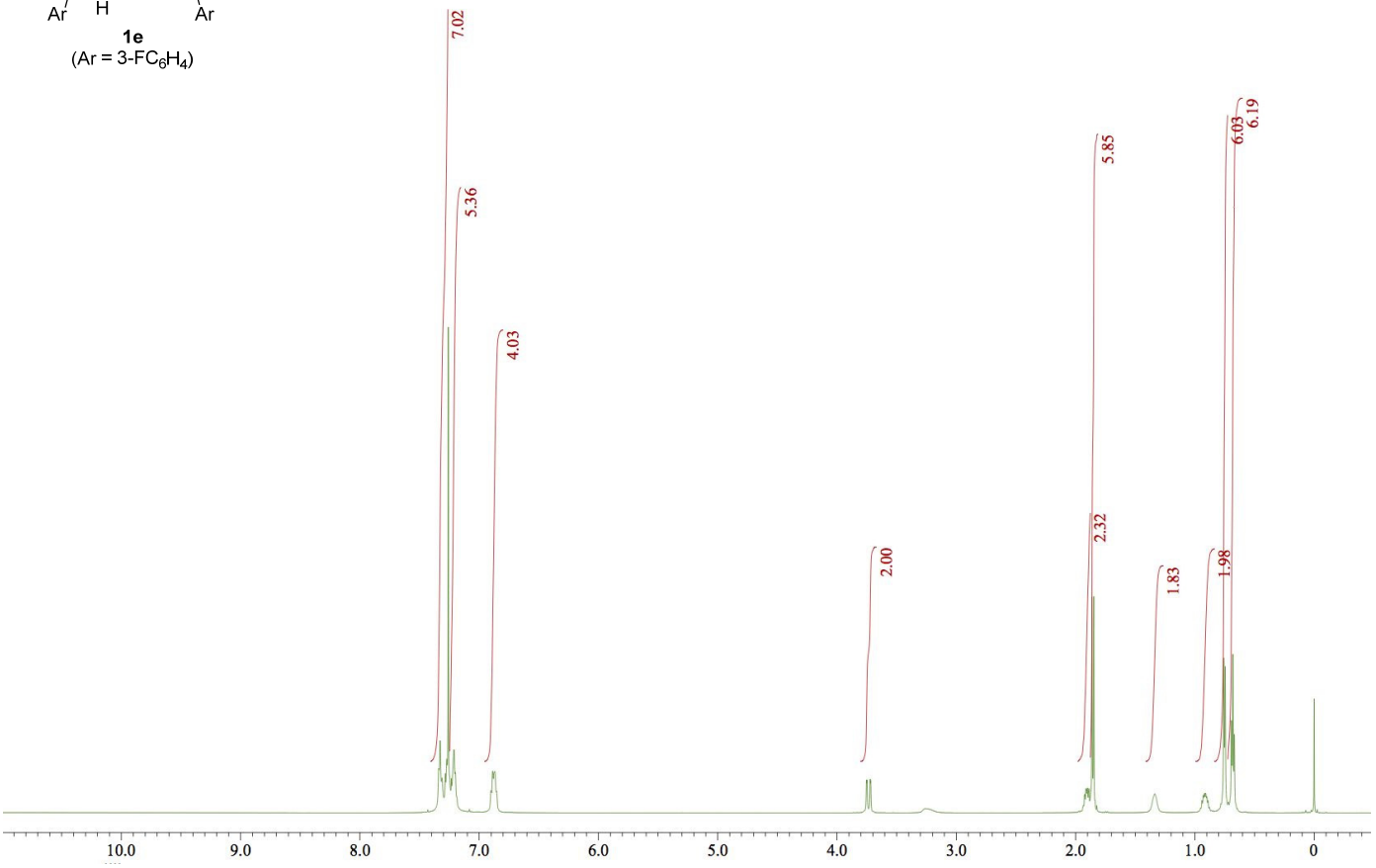


1e·HCl
(Ar = 3-FC_6H_4)




Me
Me
N
N
P
Ar
Ar
N
H
N
Ar
Ar

1e
(Ar = 3-FC_6H_4)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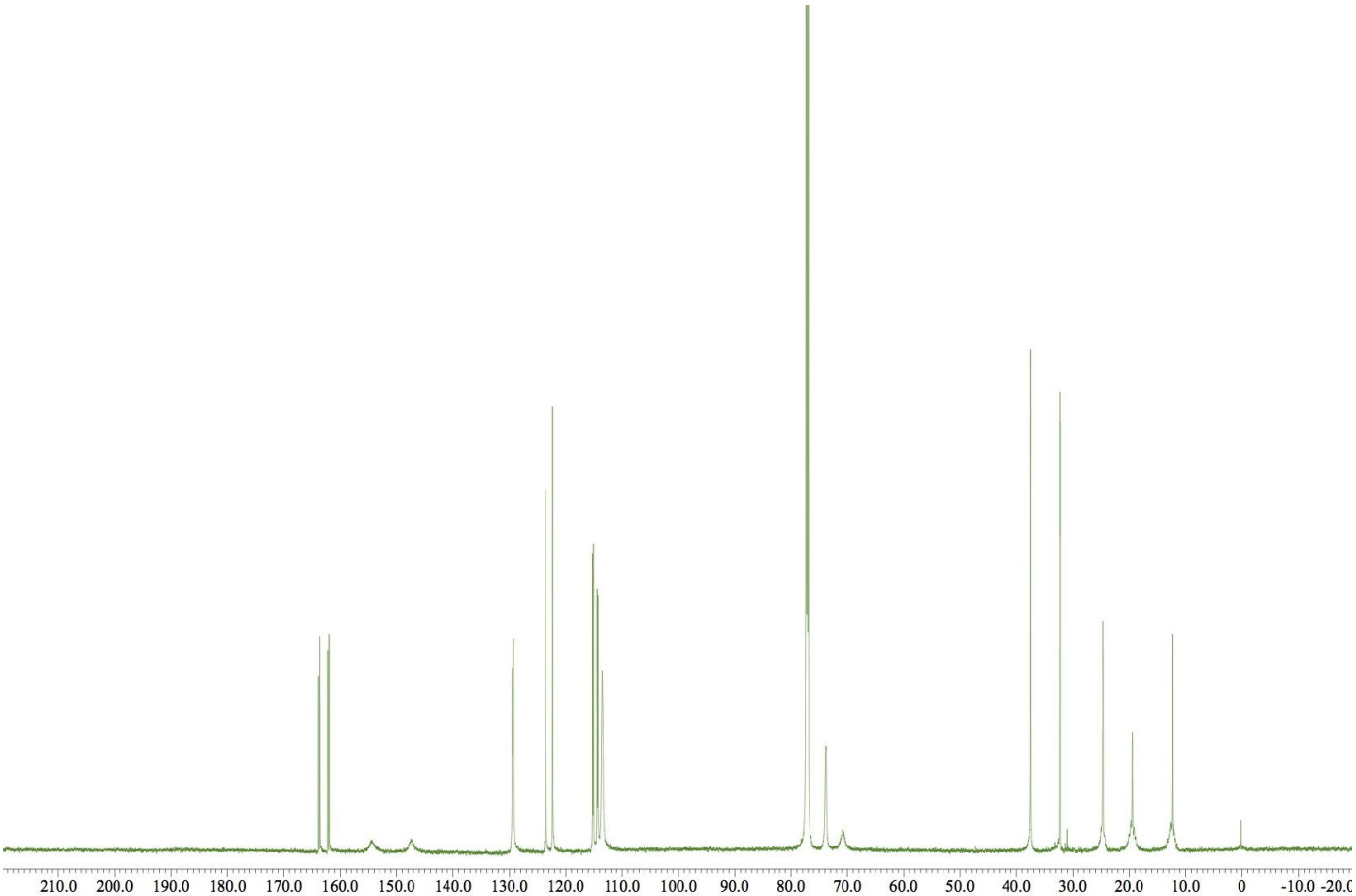
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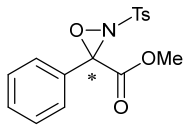
Ts
O
N
OMe
*
O

3a

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9.0
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4.0
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2.0
1.0
0


210.0
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180.0
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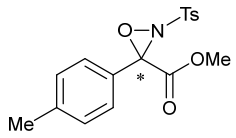
Ts
O
N
OMe
*
O
Me

3b

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1.93
1.96
3.00
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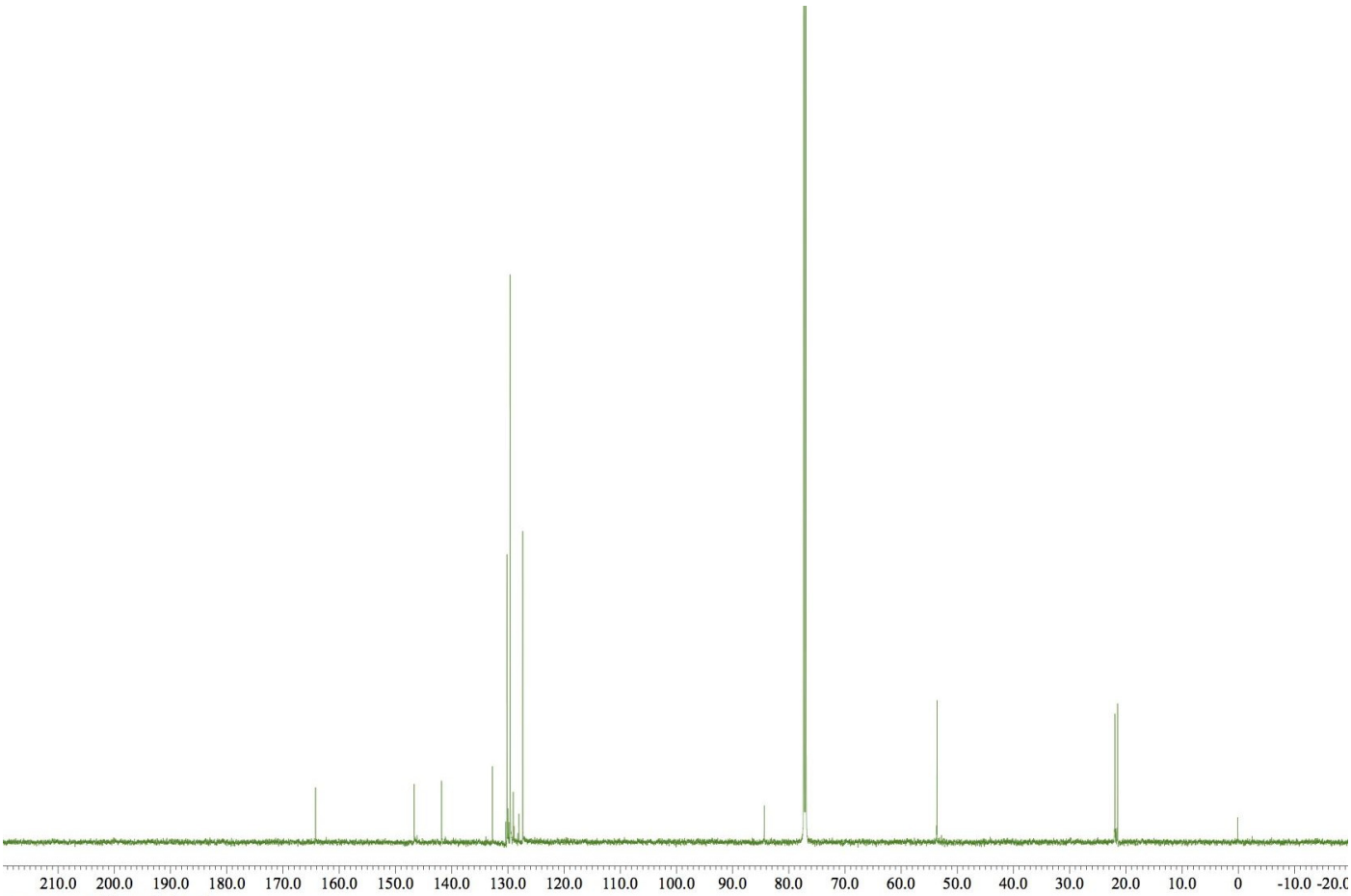
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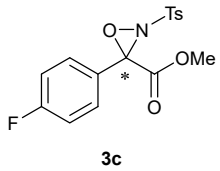
Ts
O
N
OMe
*
O
F

3c

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2.03
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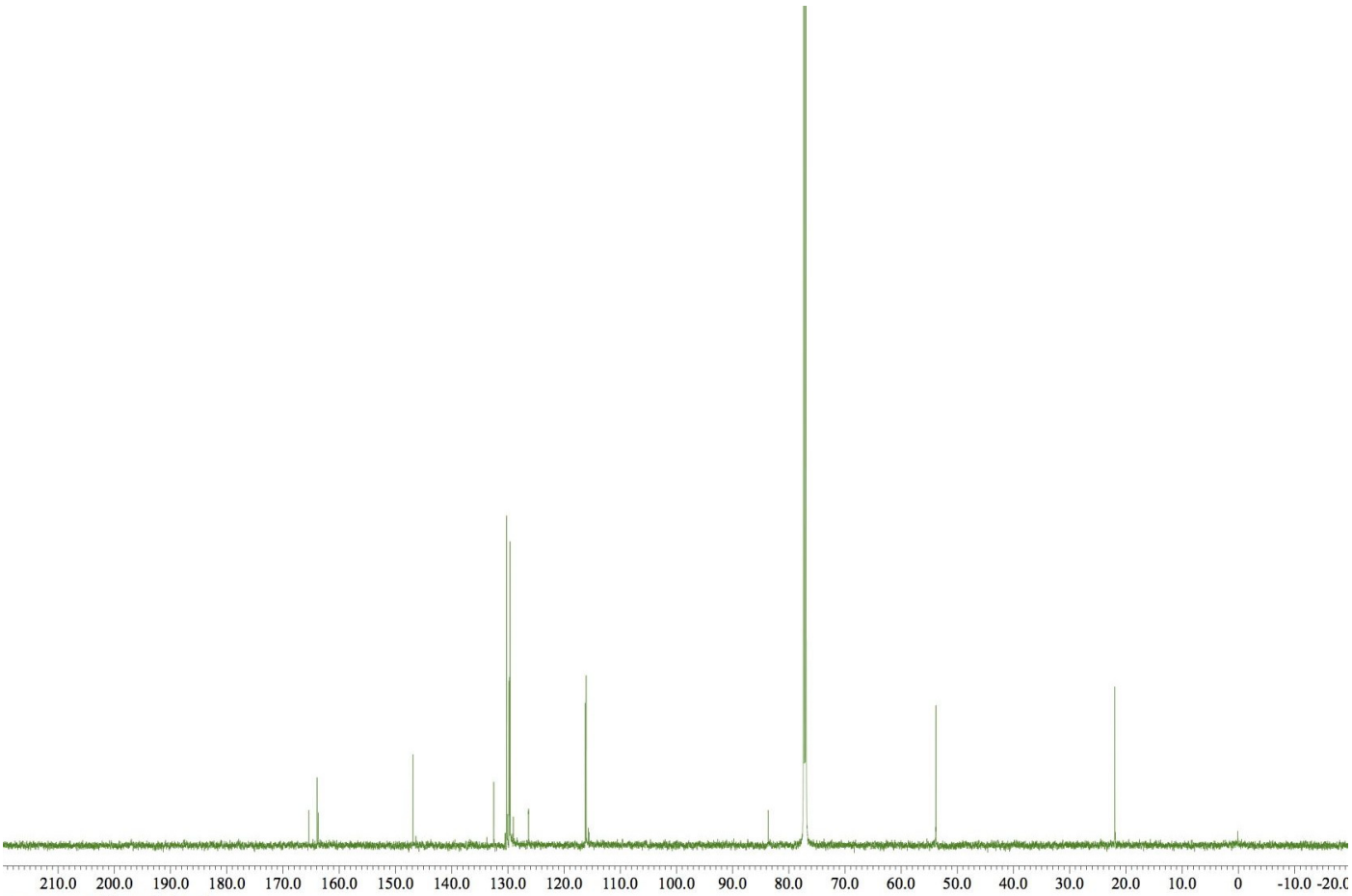
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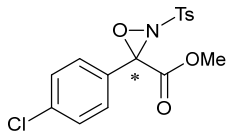
Ts
O
N
OMe
*
O
Cl

3d

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2.37
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3.00
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8.0
7.0
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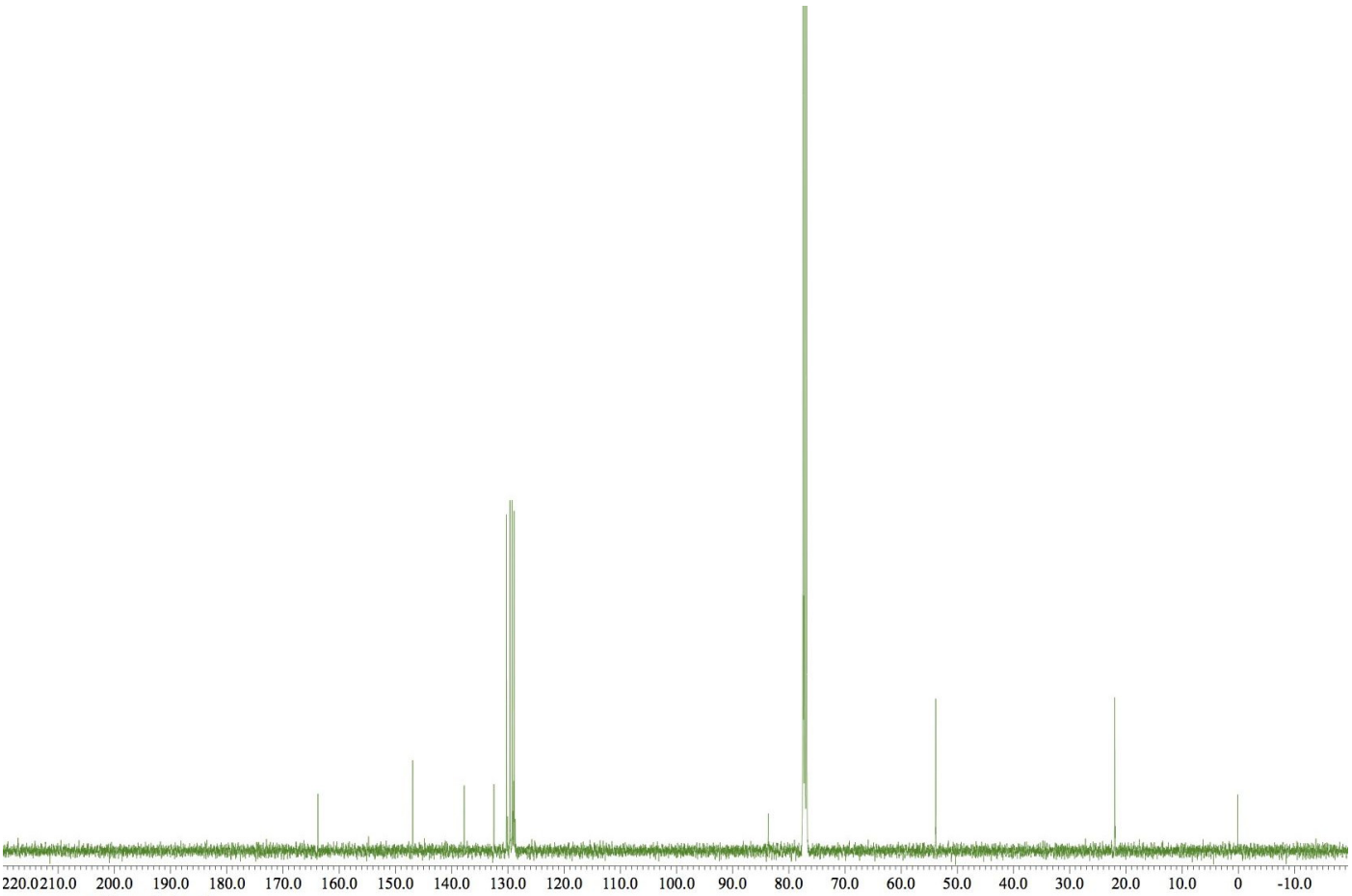
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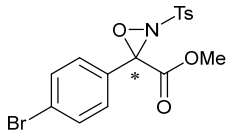
Ts
O
N
OMe
*
O
Br

3e

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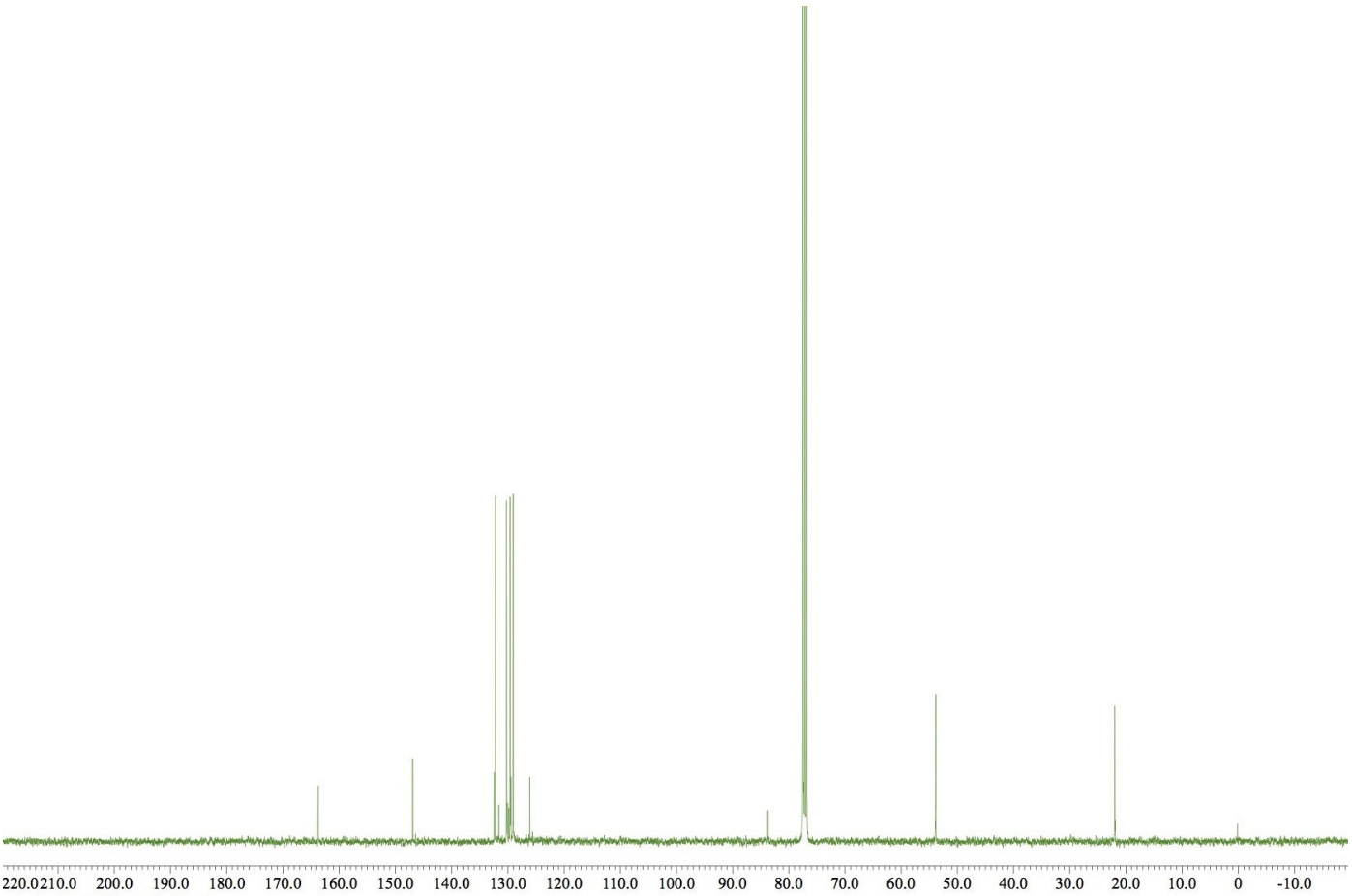
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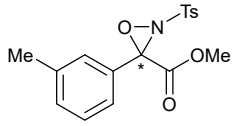
Ts
O
N
Me
OMe
*
O

3f

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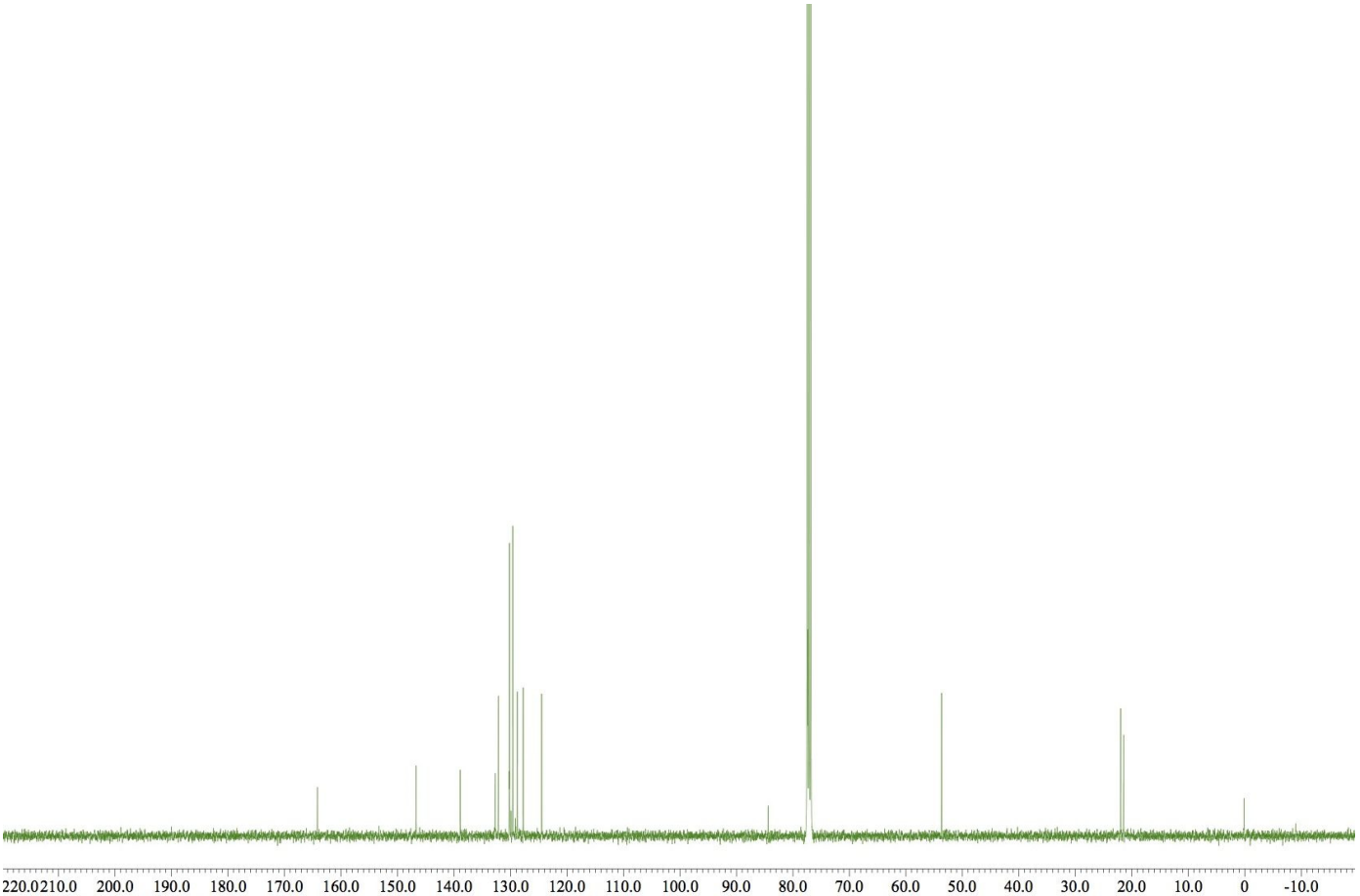
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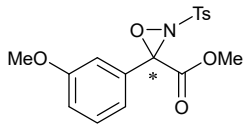
Ts
O
N
MeO
OMe
*
O

3g

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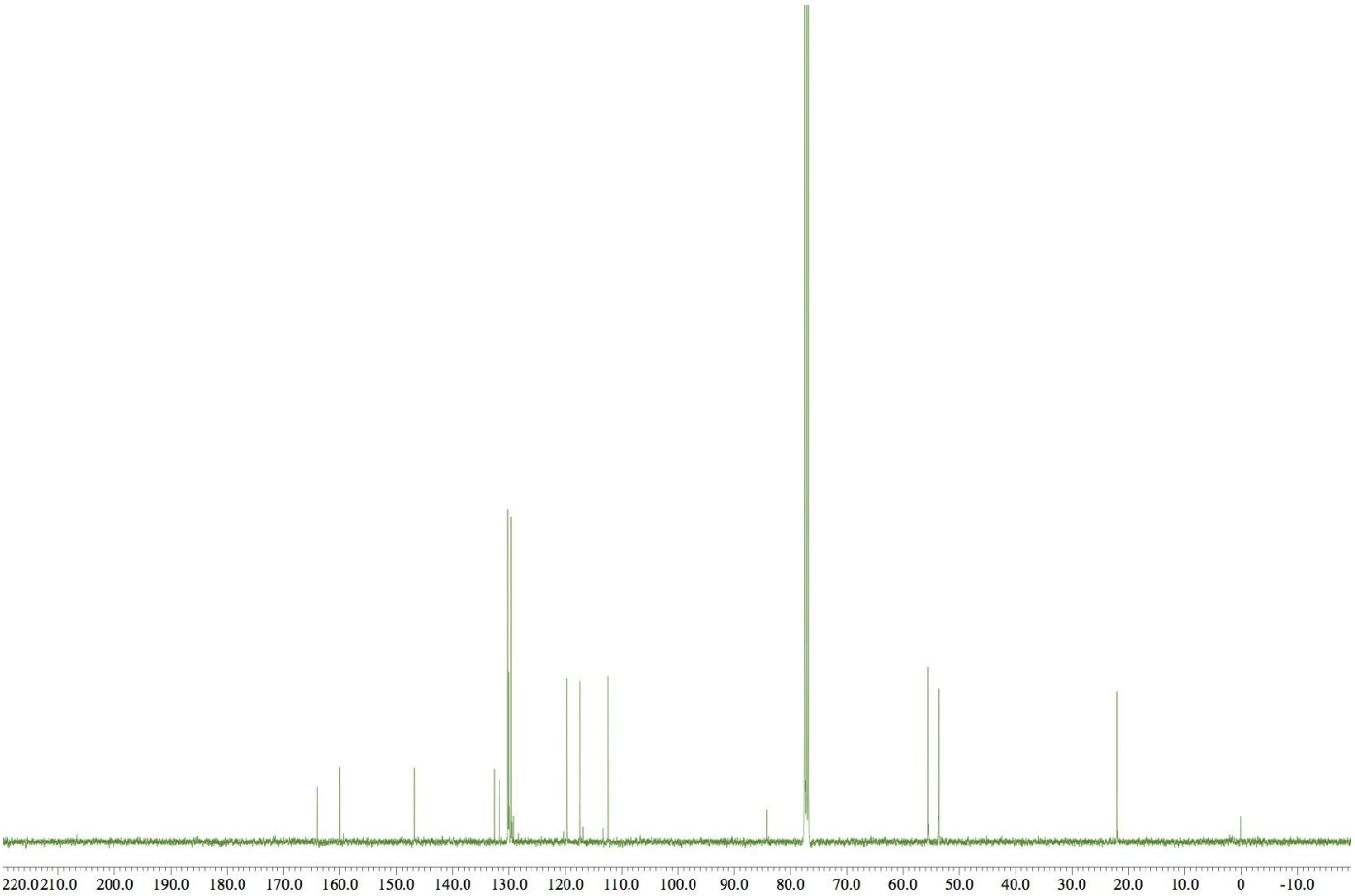
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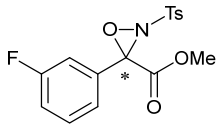
Ts
O
N
F
OMe
*
O

3h

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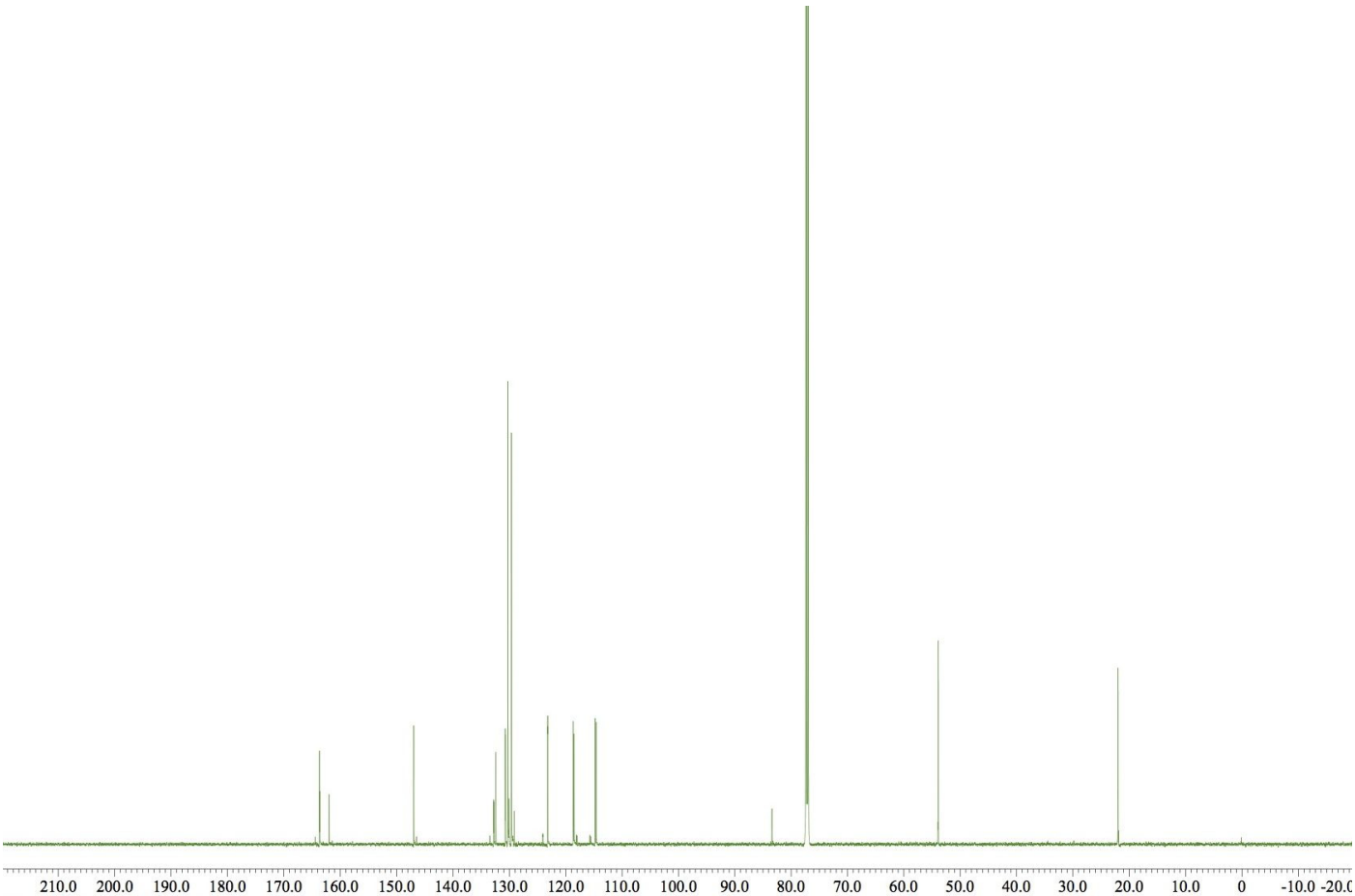
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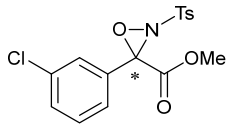
Ts
O
N
Cl
OMe
*
O

3i

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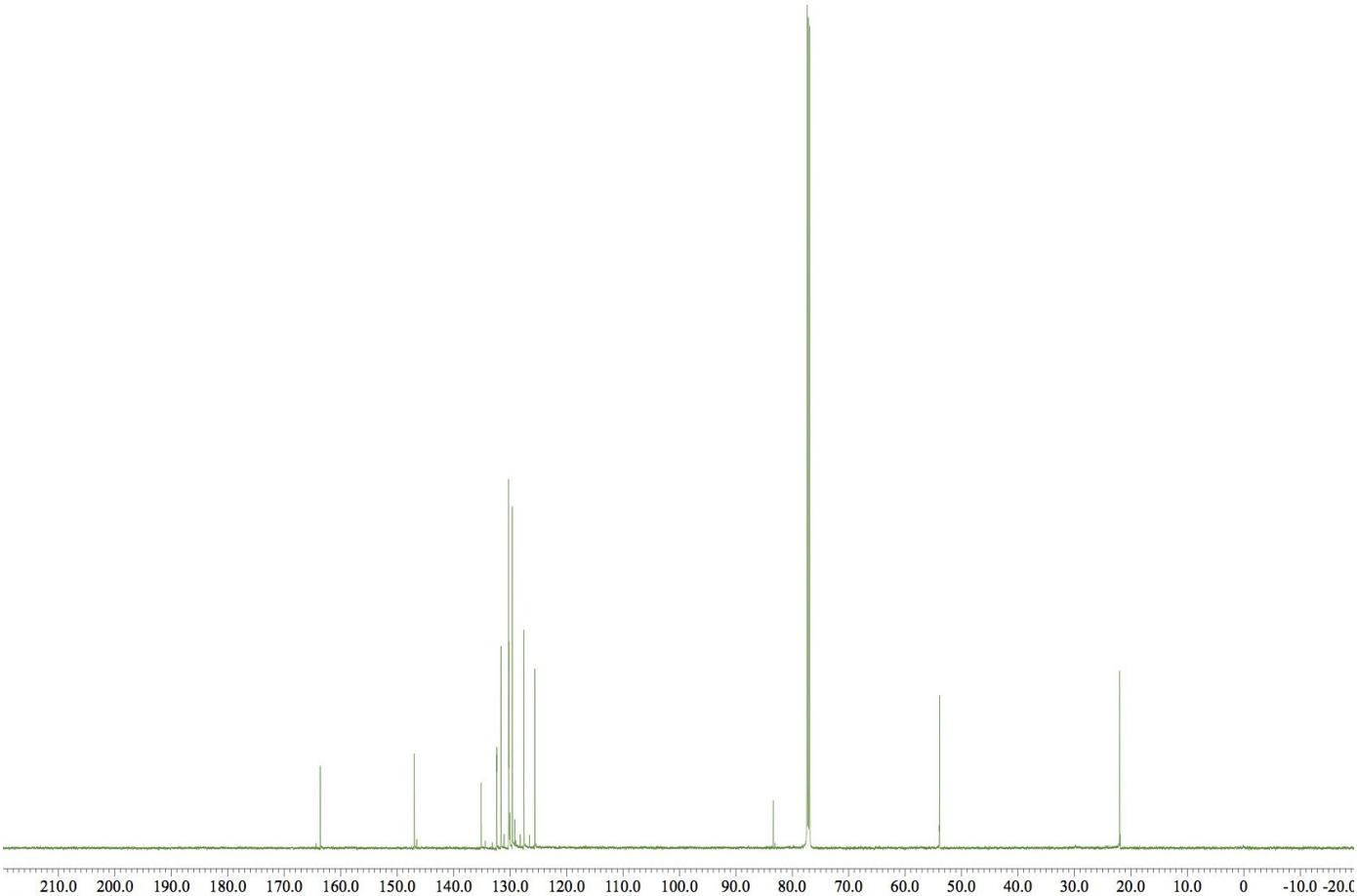
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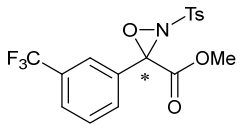
Ts
O
N
F3C
OMe
*
O

3j

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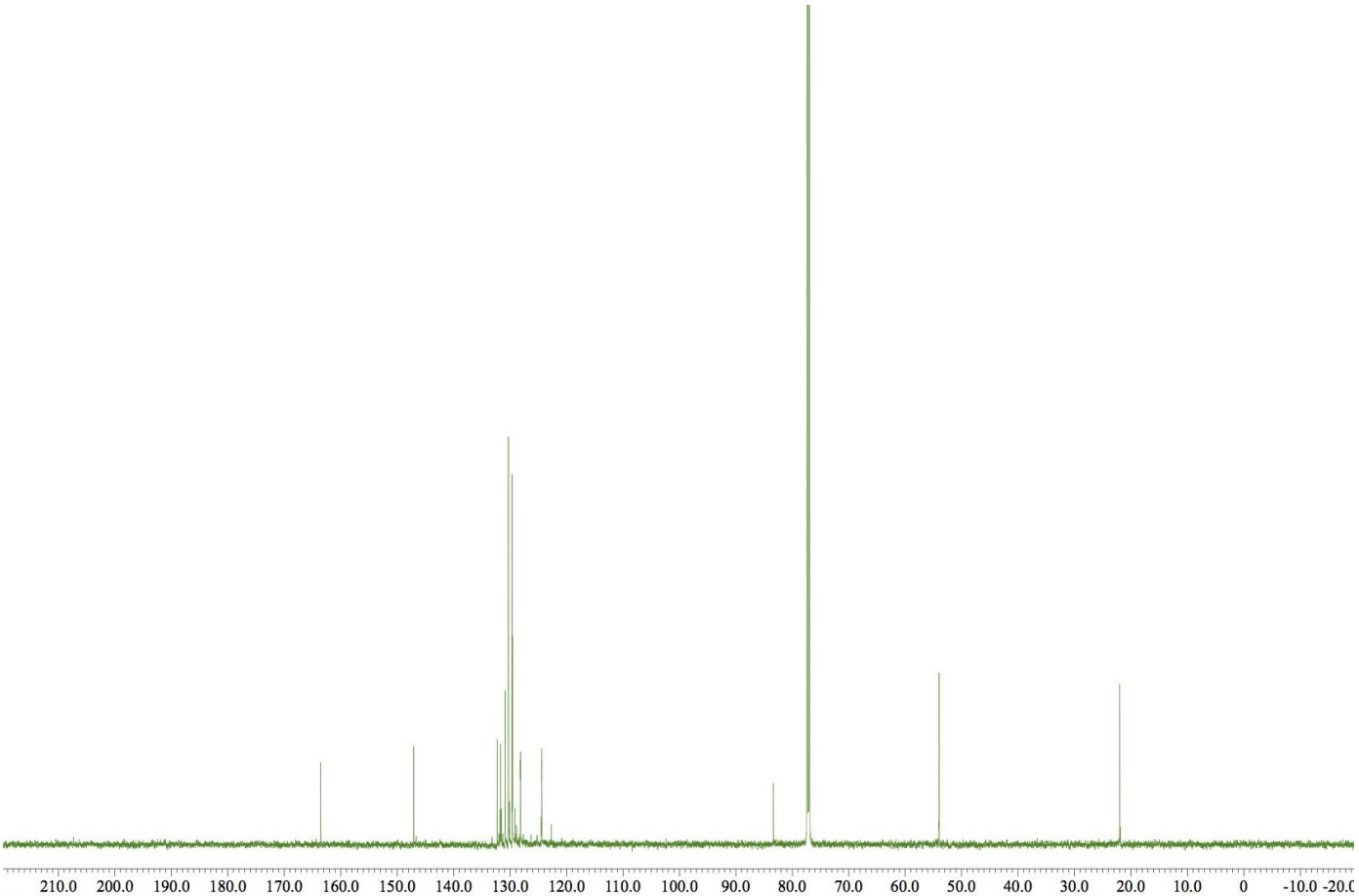
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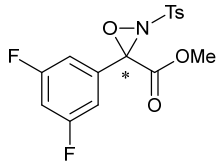
Ts
O
N
F
OMe
*
O
F

3k

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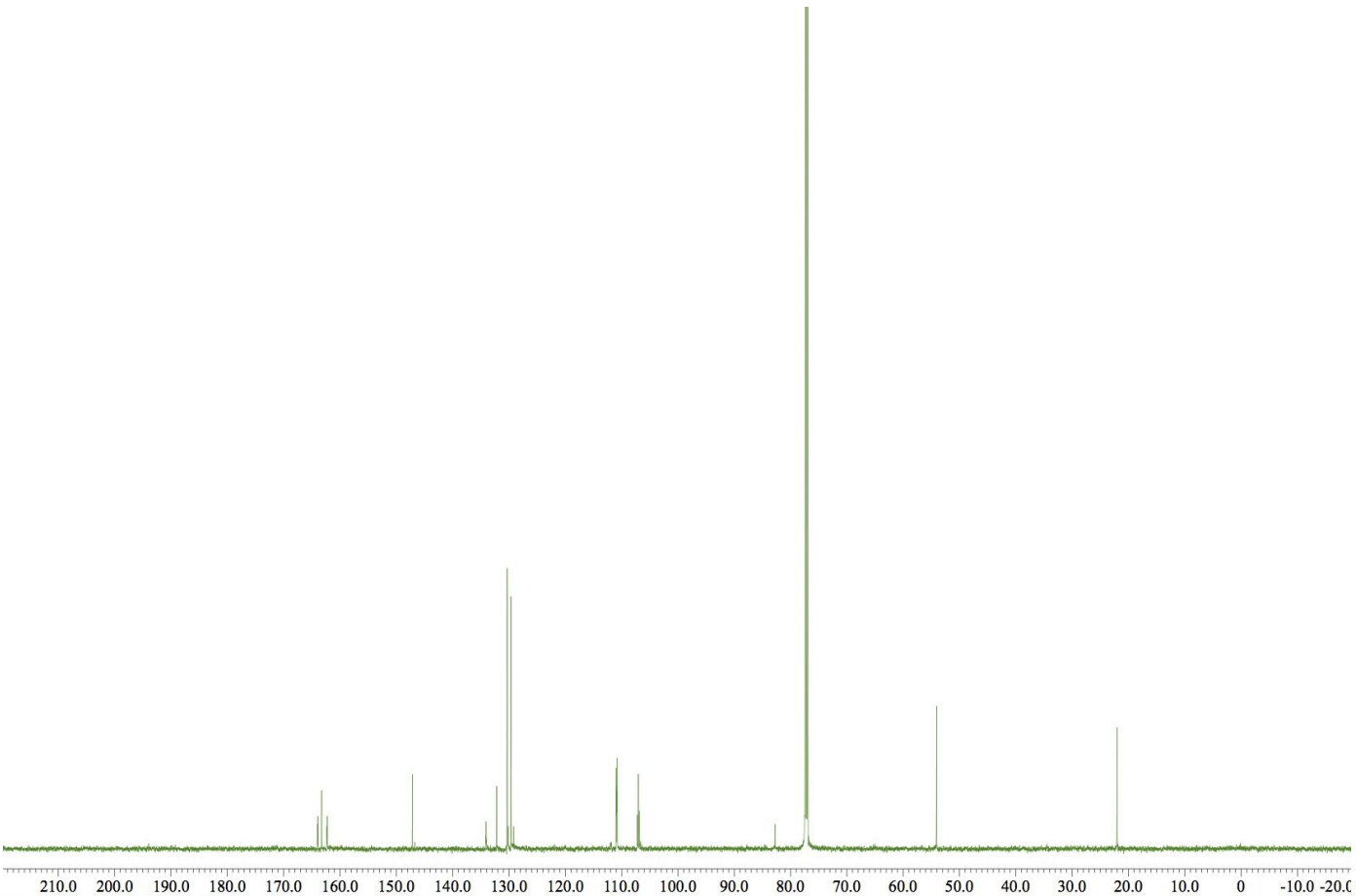
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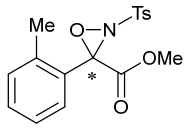
Me
O
N
Ts
OMe
*
O

3l

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3.00
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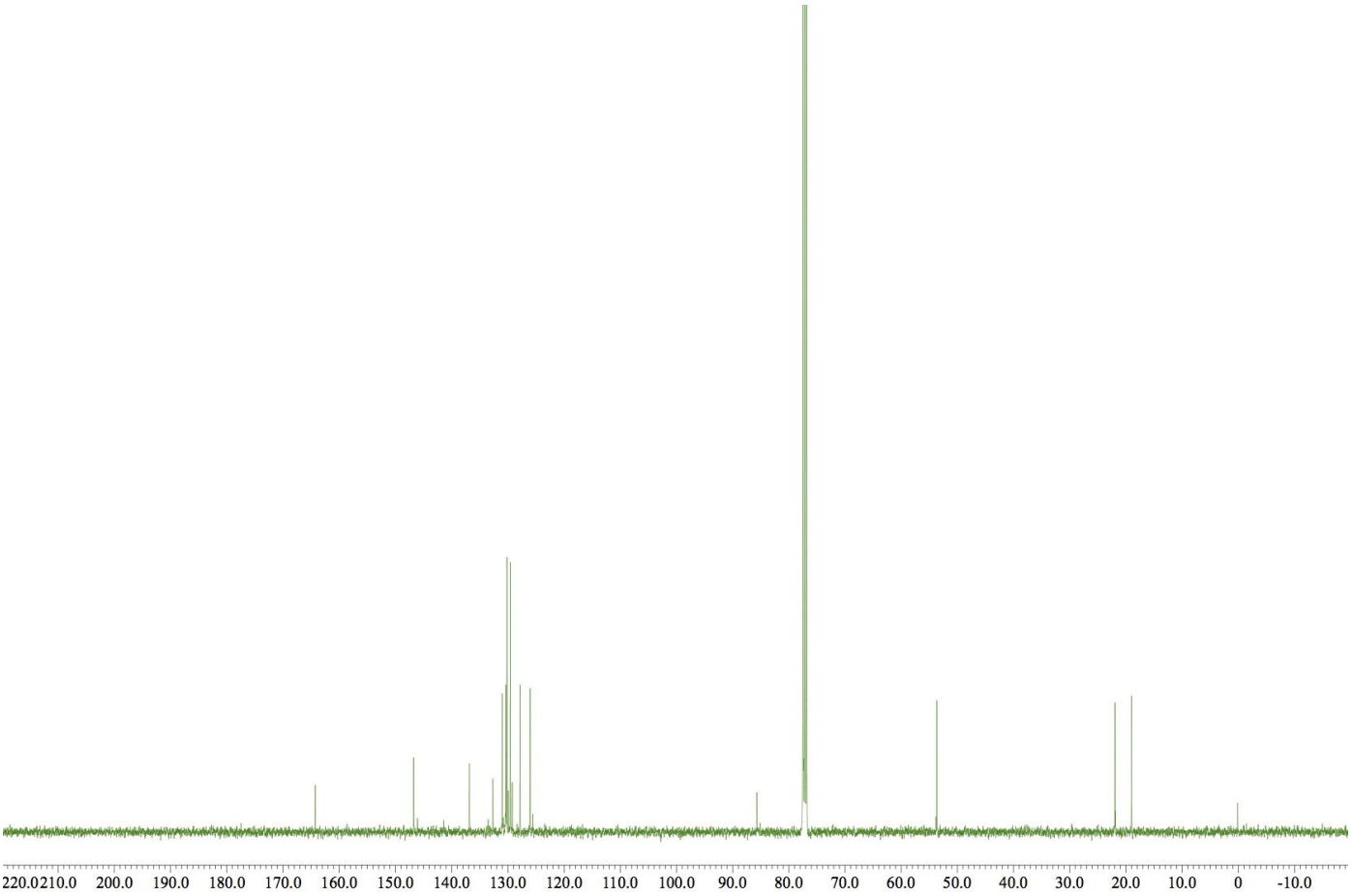
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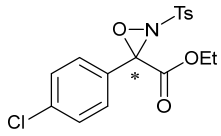
Ts
O
N
OEt
*
O
Cl

3m

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0


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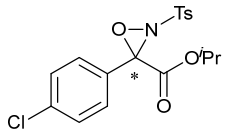
Ts
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iPr
*
Cl

3n

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2.18
1.00
3.06
3.01
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1.0
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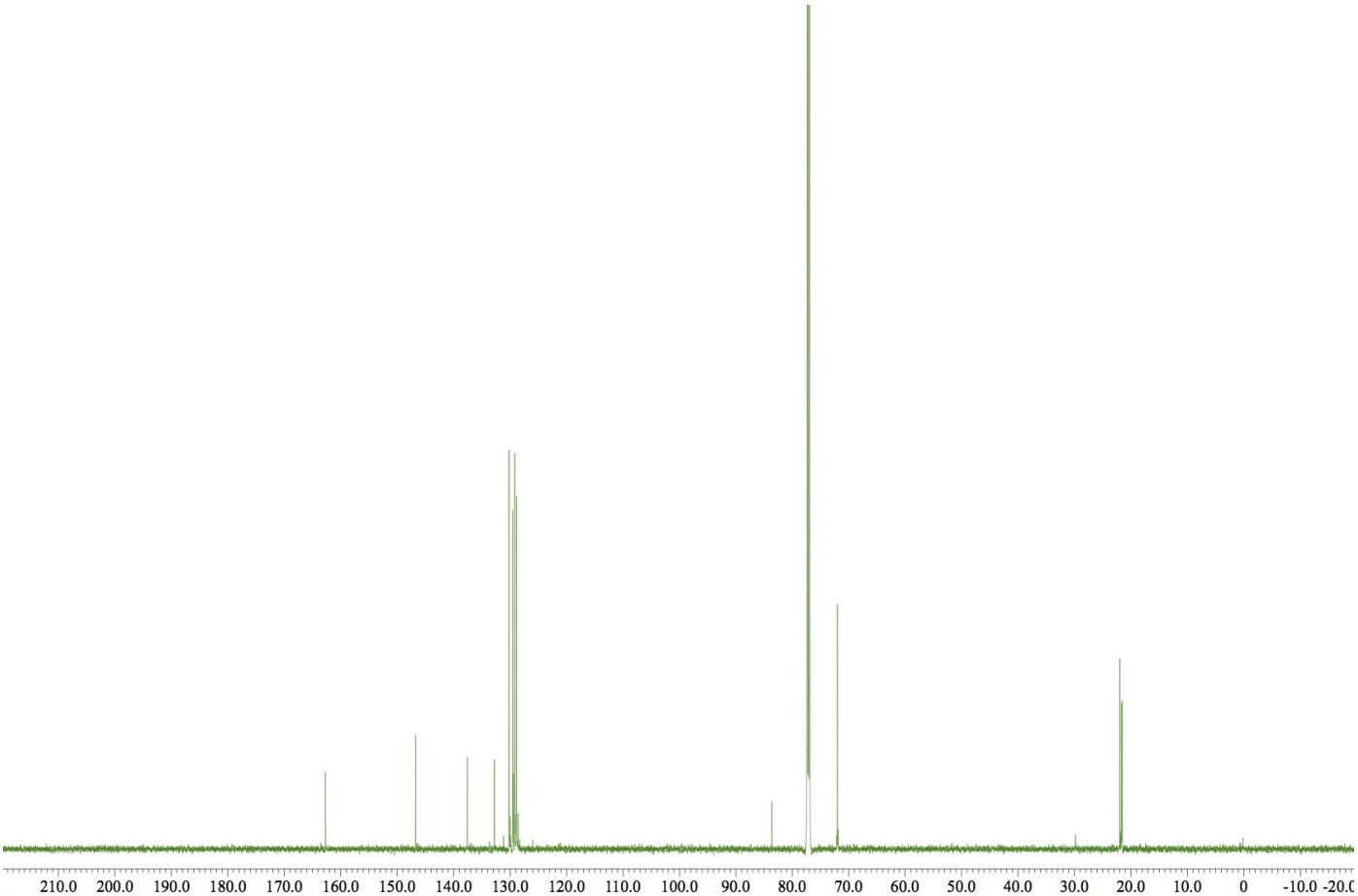
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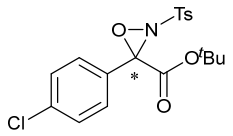
Ts
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O
tBu
*
O
Cl

3o

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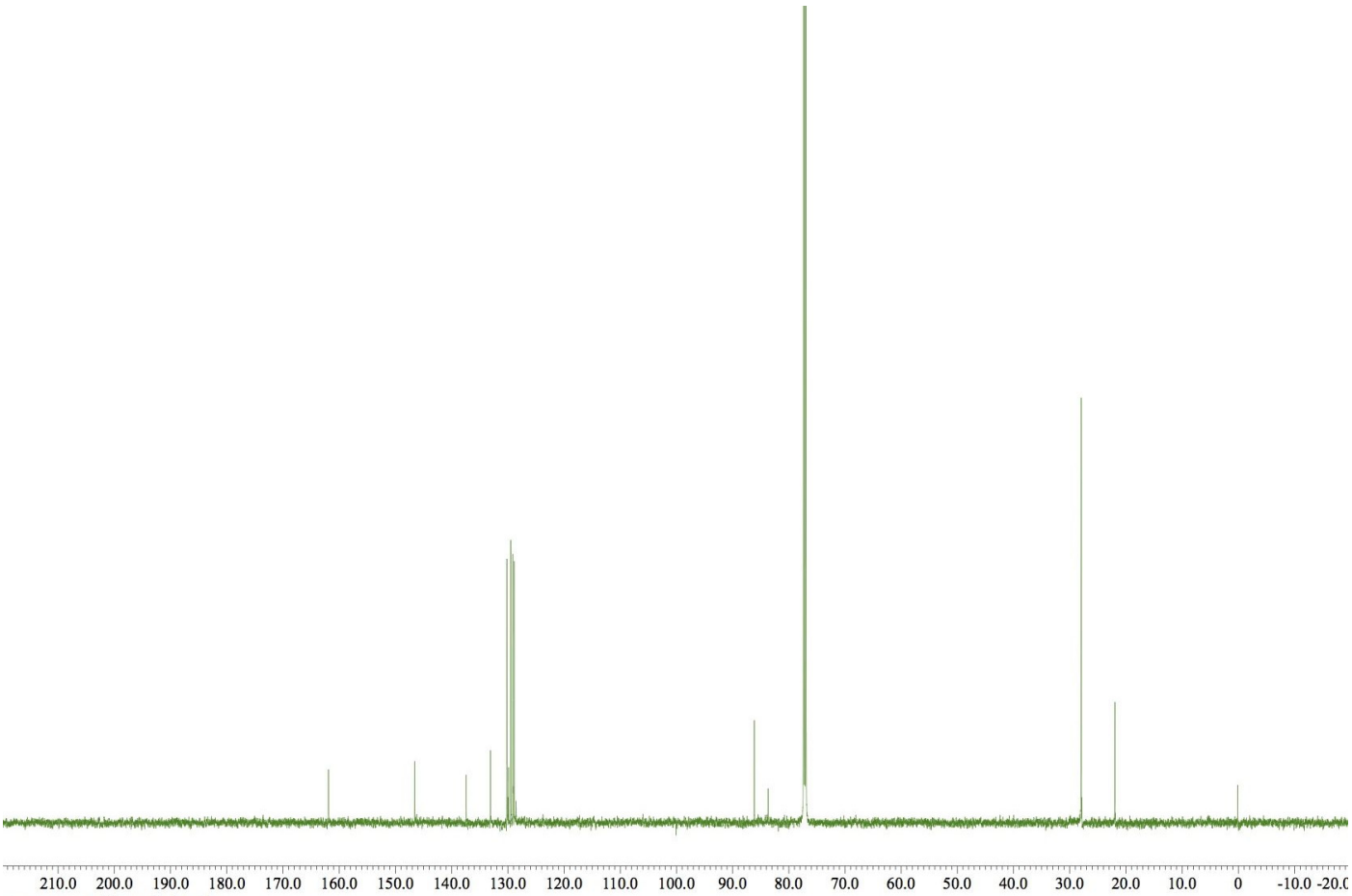
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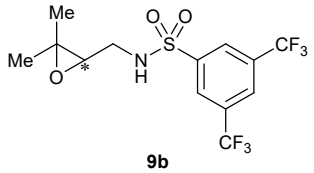
Me
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O
S
N
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CF3
CF3

9b

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1.07
1.03
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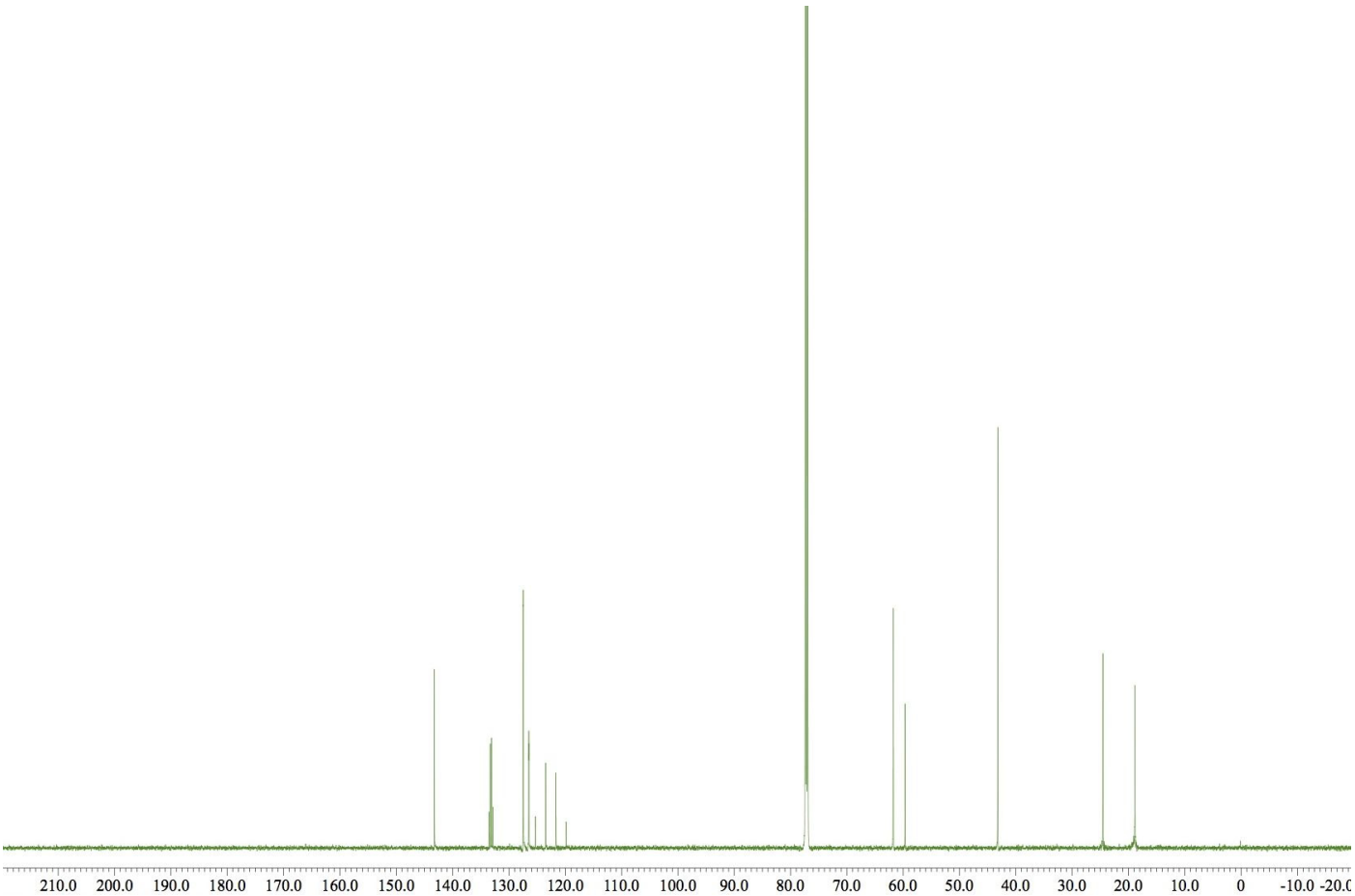
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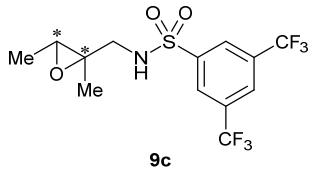
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N
H
O
O
S
CF3
CF3

9c

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1.00
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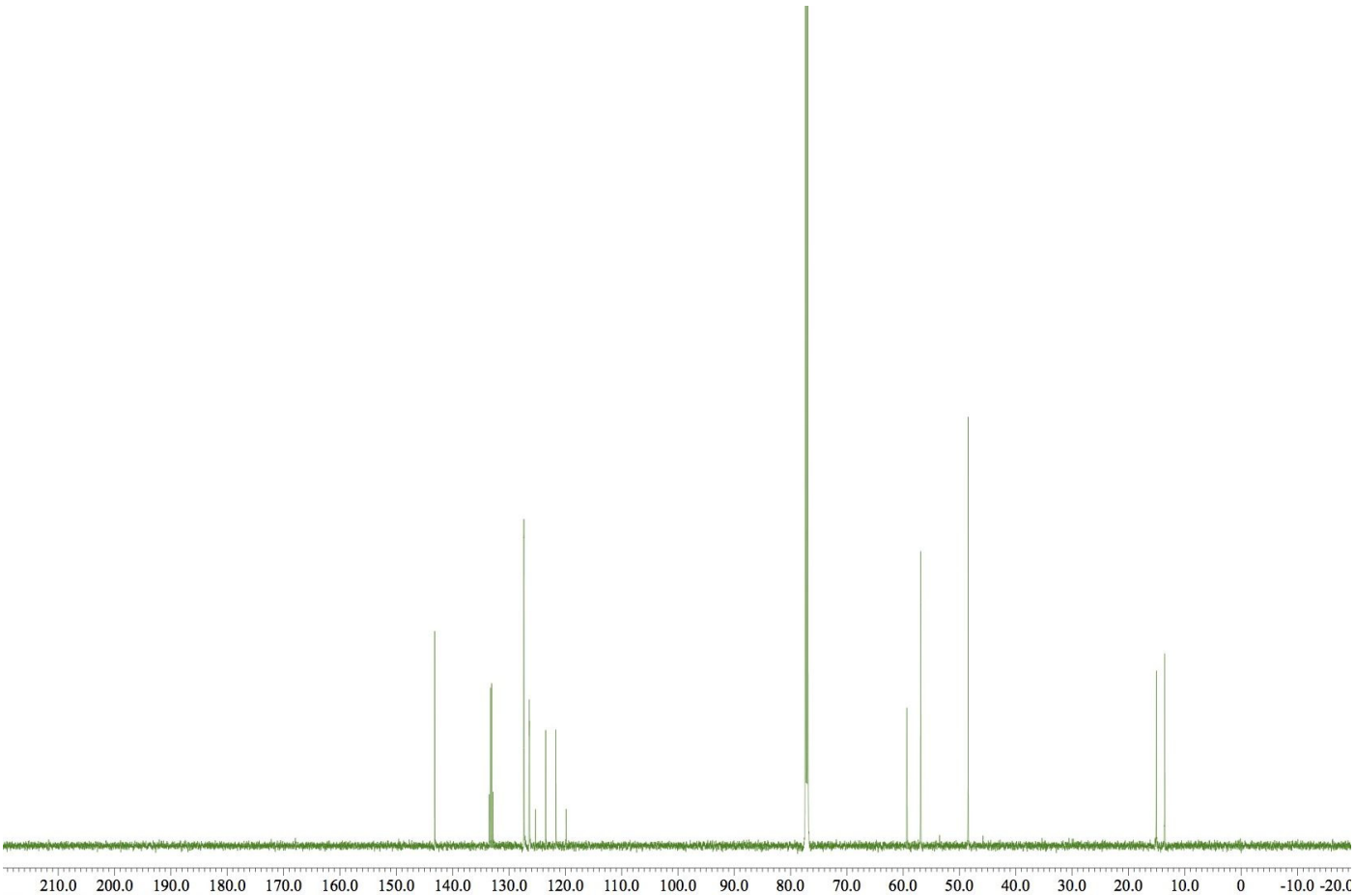
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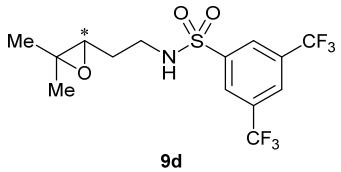
Me
Me
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N
H
S
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CF3
CF3

9d

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1.04
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0.95
3.06
3.05
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7.0
6.0
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4.0
3.0
2.0
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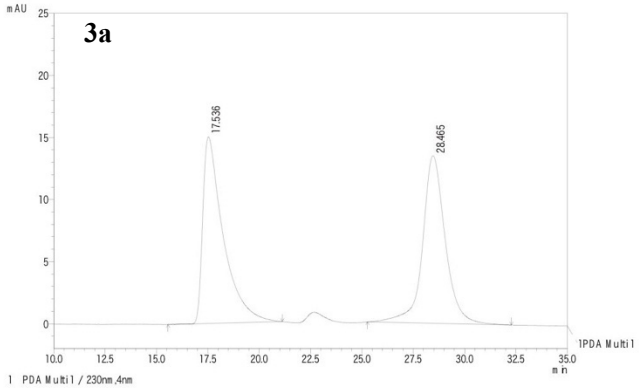
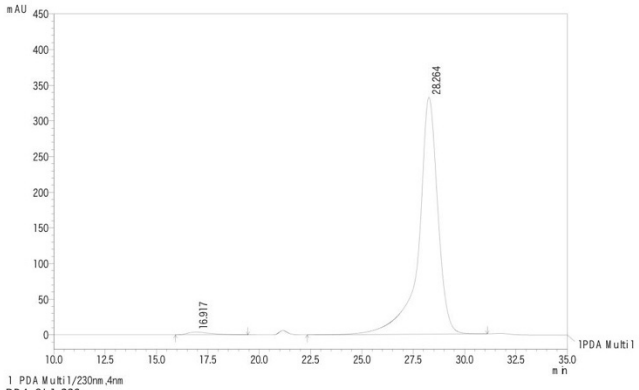
HPLC traces

3a

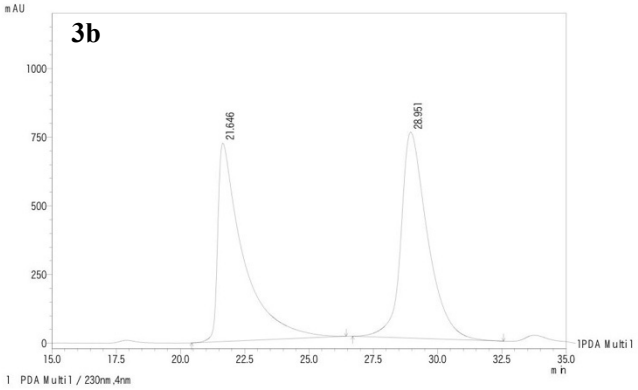


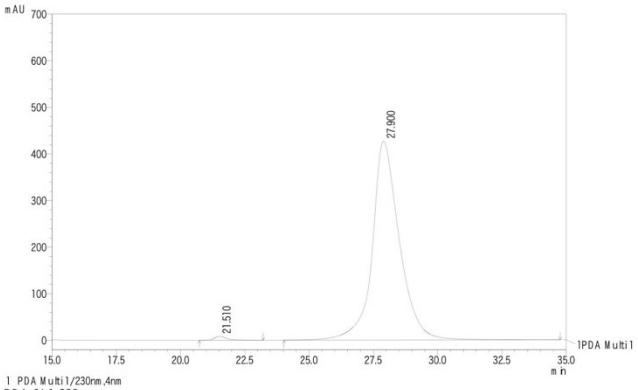


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	16.917	1.419
2	28.264	98.581
合計		100.000

3b

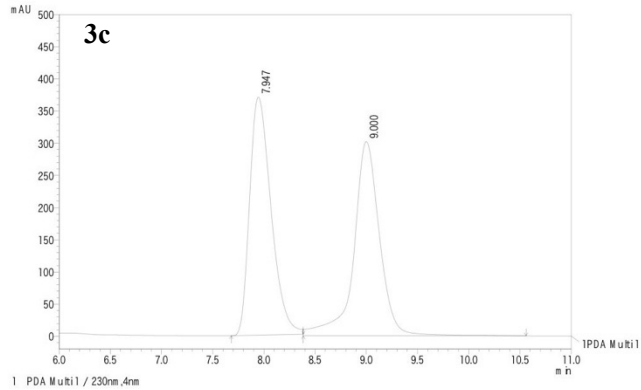


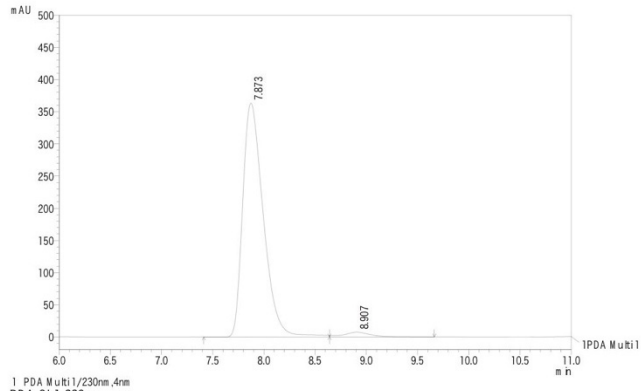


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	21.510	0.844
2	27.900	99.156
合計		100.000

3c

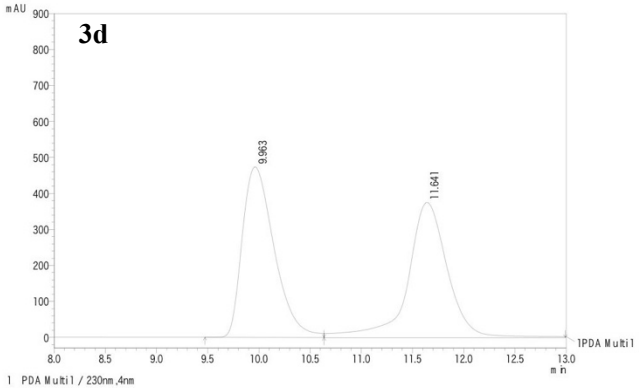


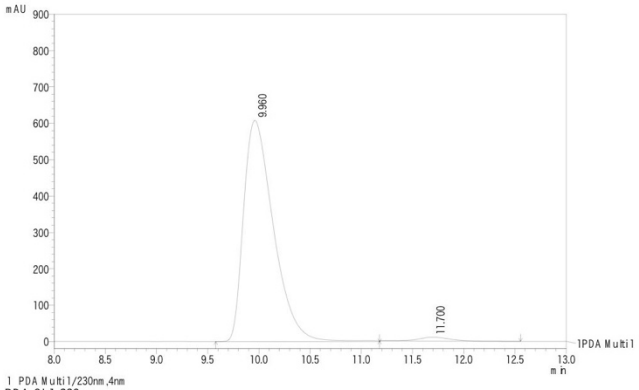


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	7.873	97.422
2	8.907	2.578
合計		100.000

3d

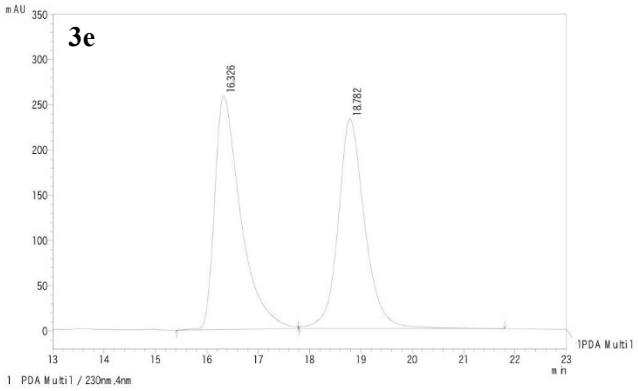


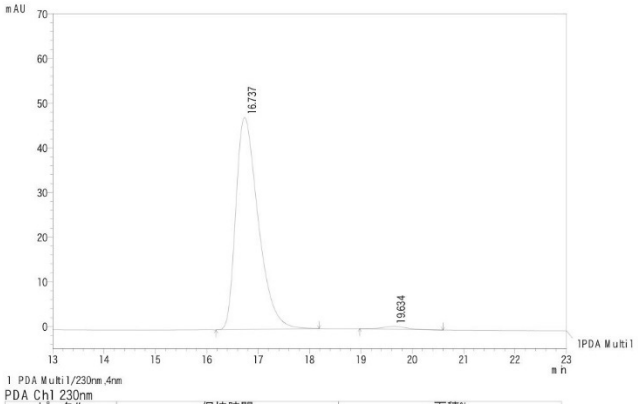


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	9.960	97.954
2	11.700	2.046
合計		100.000

3e

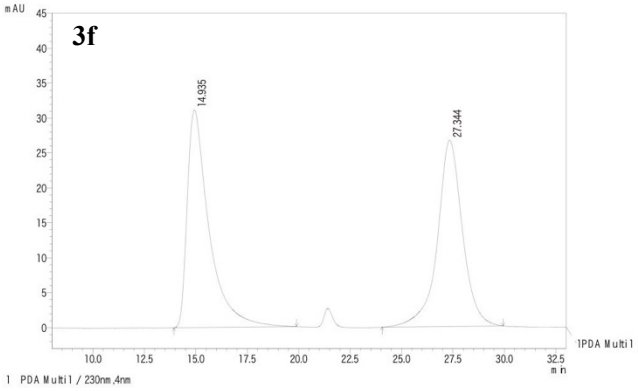


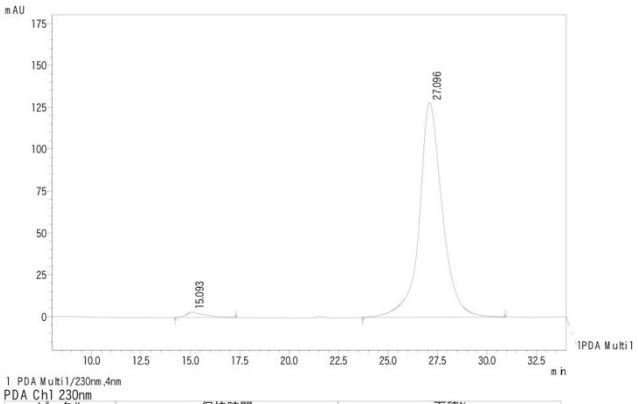


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	16.737	98.632
2	19.634	1.368
合計		100.000

3f

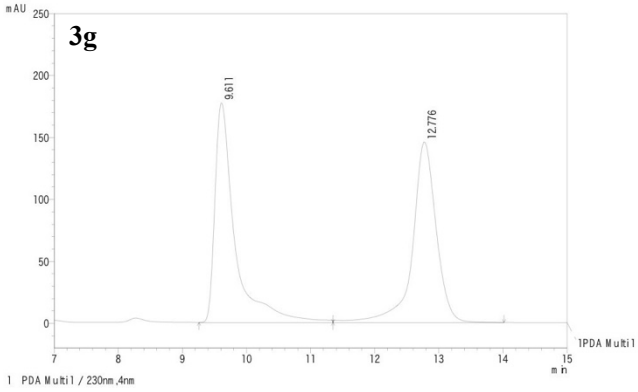


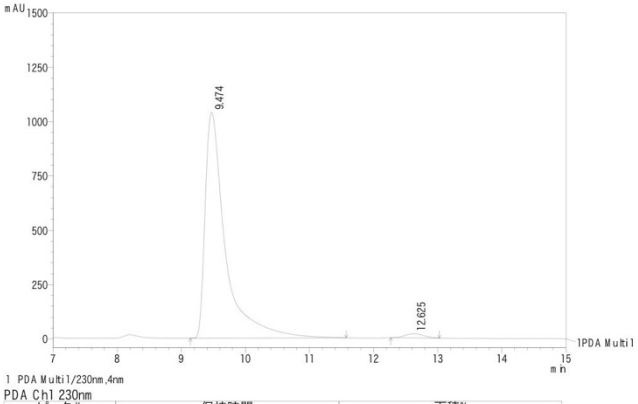


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	15.093	1.996
2	27.096	98.004
合計		100.000

3g

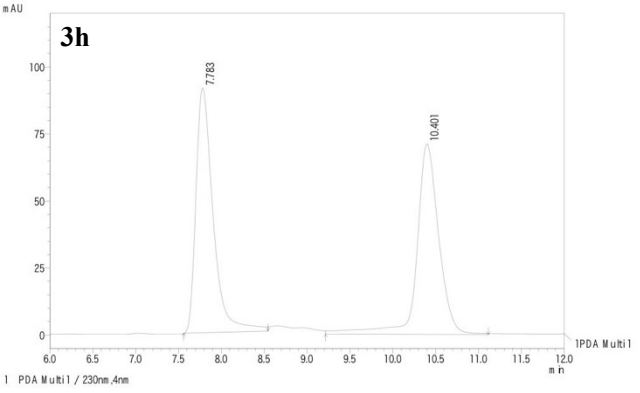


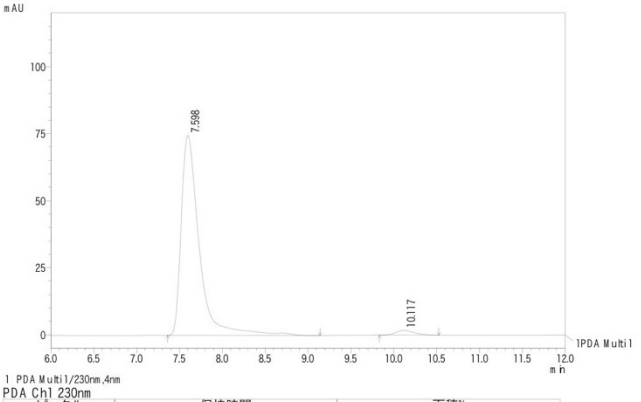


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	9.474	98.315
2	12.625	1.685
合計		100.000

3h

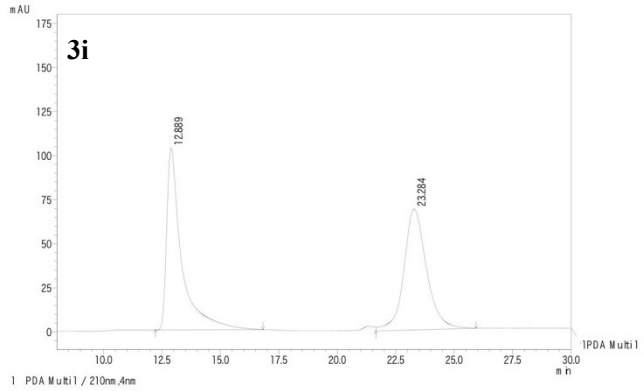


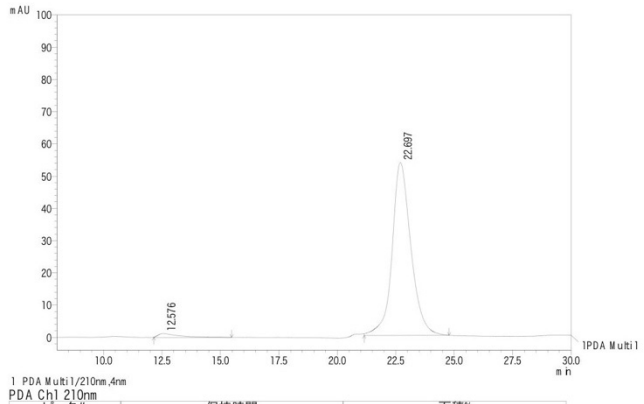


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	7.598	97.637
2	10.117	2.363
合計		100.000

3i

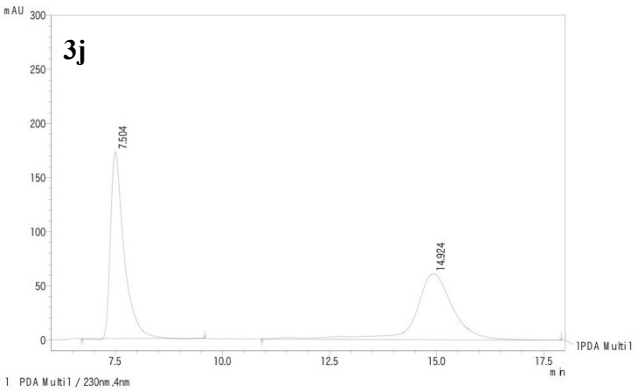


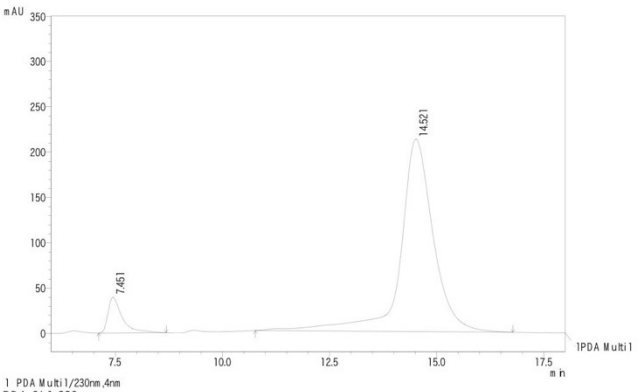


PDA Ch1 210nm

ピーク#	保持時間	面積%
1	12.576	2.371
2	22.697	97.629
合計		100.000

3j

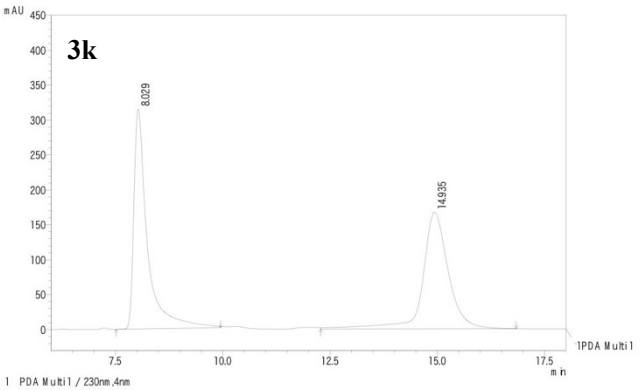


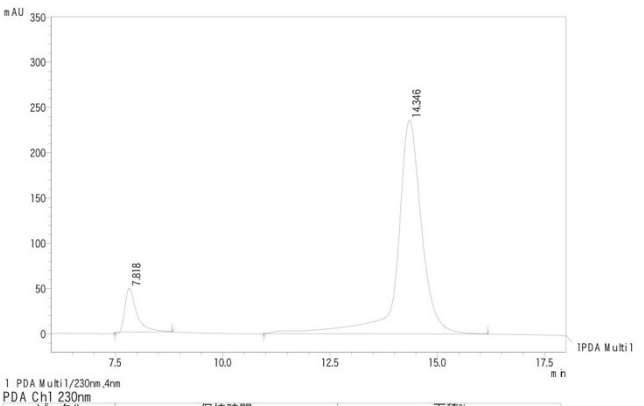


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	7.451	7.423
2	14.521	92.577
合計		100.000

3k

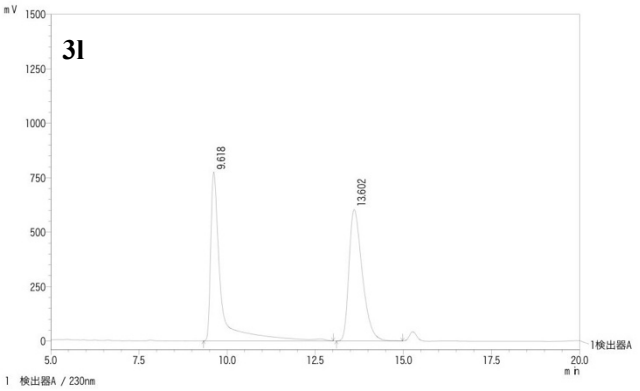


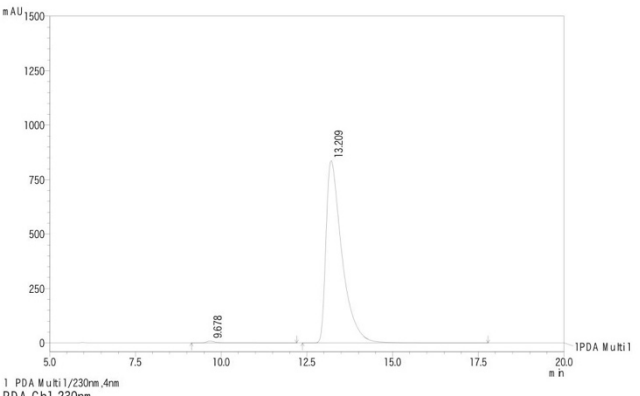


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	7.818	8.977
2	14.346	91.023
合計		100.000

3l

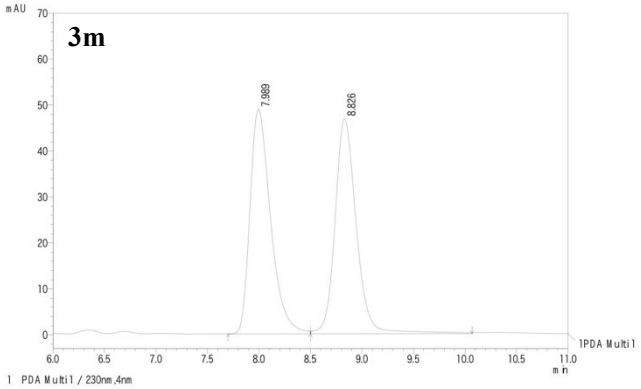


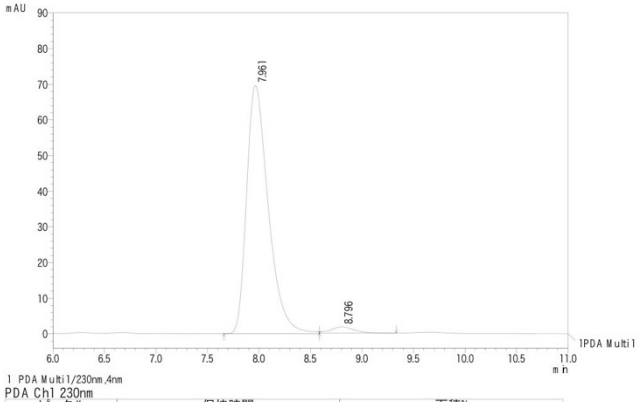


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	9.678	0.735
2	13.209	99.265
合計		100.000

3m

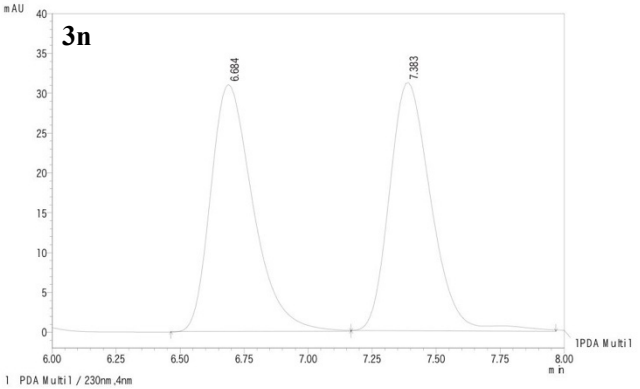


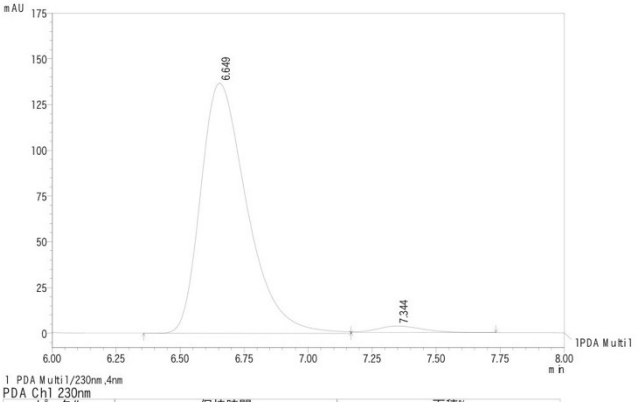


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	7.961	97.338
2	8.796	2.662
合計		100.000

3n

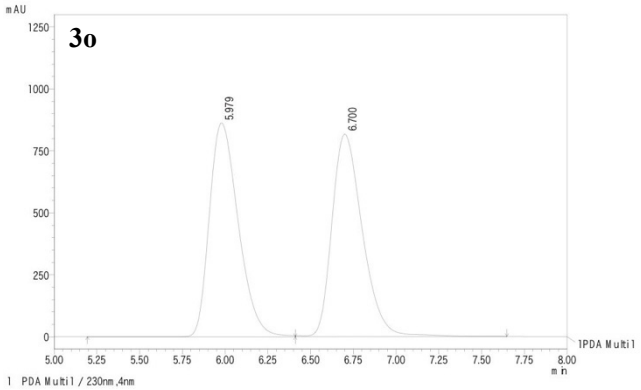


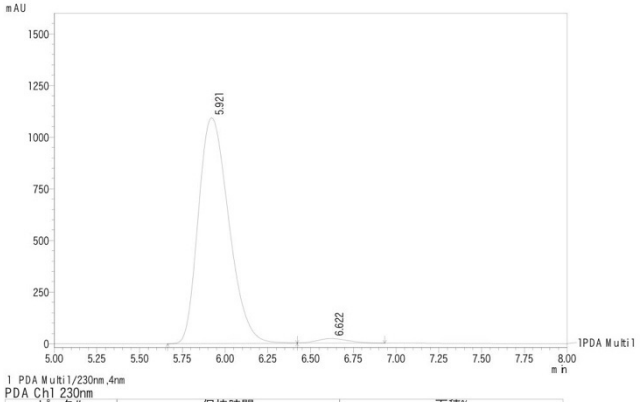


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	6.649	97.443
2	7.344	2.557
合計		100.000

3o

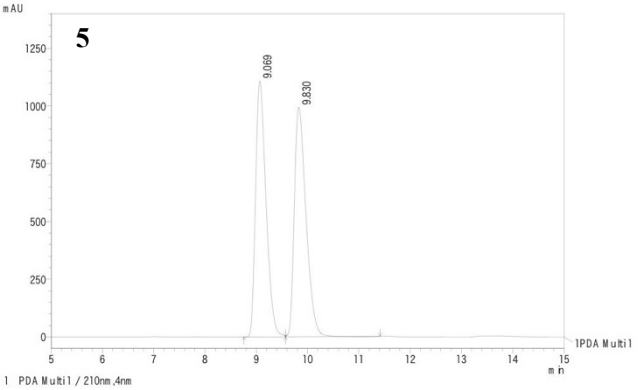


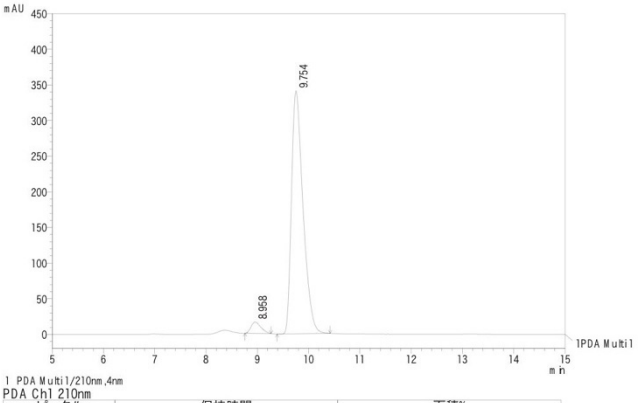


PDA Ch1 230nm

ピーク#	保持時間	面積%
1	5.921	97.865
2	6.622	2.135
合計		100.000

5

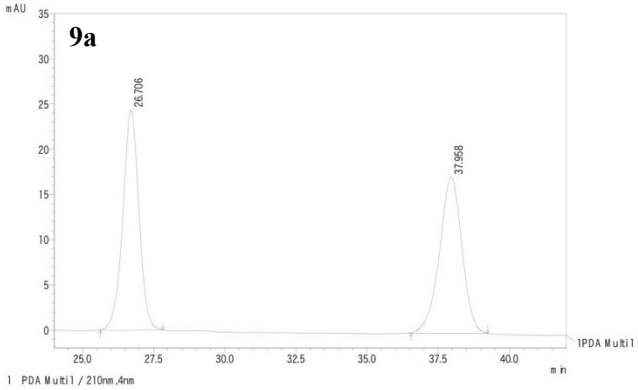


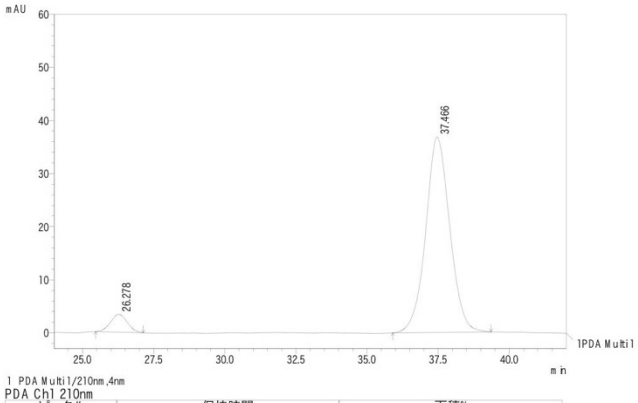


PDA Ch1 210nm

ピーク#	保持時間	面積%
1	8.958	3.886
2	9.754	96.114
合計		100.000

9a

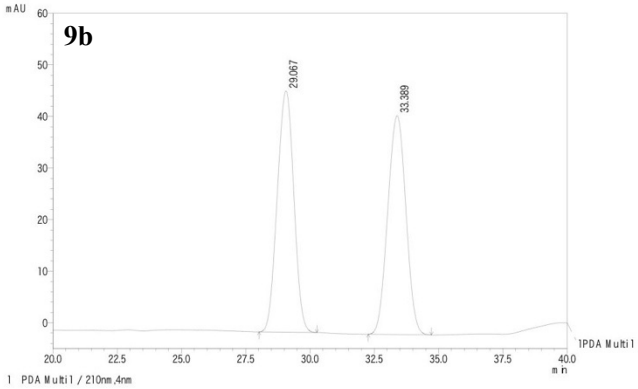


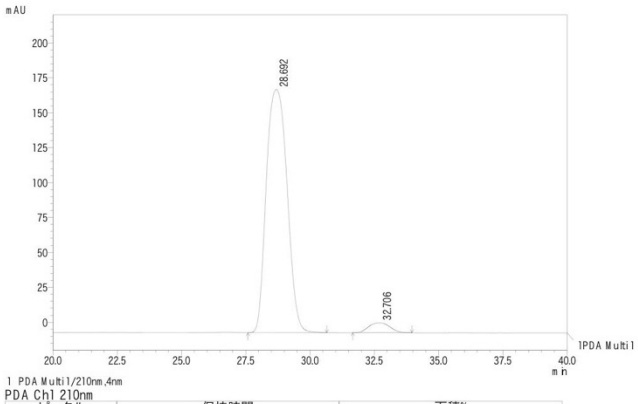


PDA Ch1 210nm

ピーク#	保持時間	面積%
1	26.278	5.965
2	37.466	94.035
合計		100.000

9b

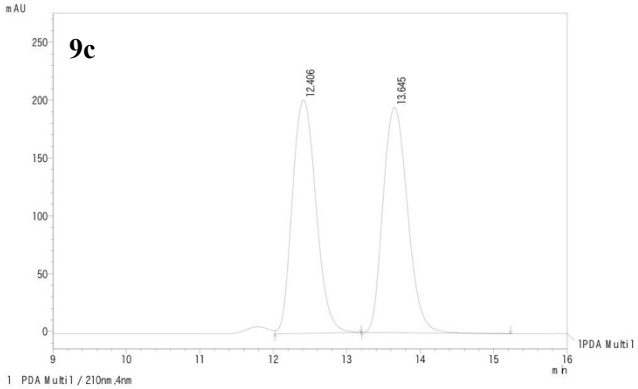


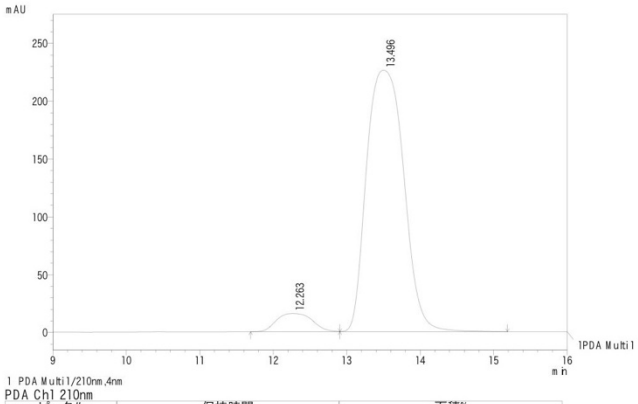


PDA Ch1 210nm

ピーク#	保持時間	面積%
1	28.692	95.971
2	32.706	4.029
合計		100.000

9c

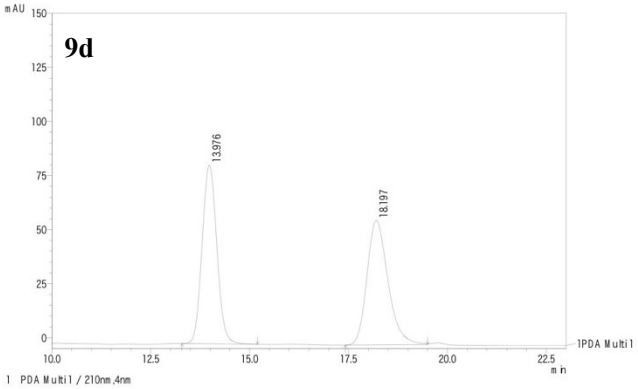


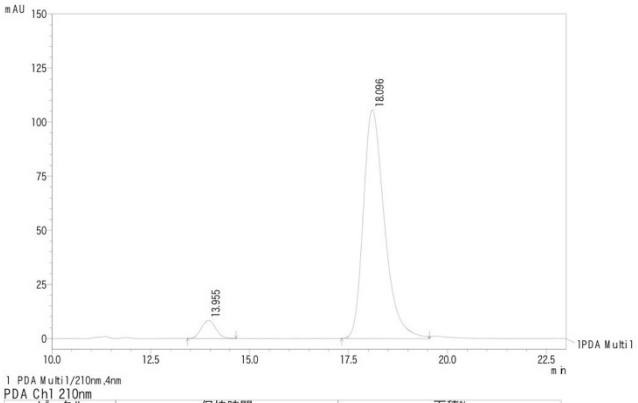


PDA Ch1 210nm

ピーク#	保持時間	面積%
1	12.263	6.251
2	13.496	93.749
合計		100.000

9d





PDA Ch1 210nm

ピーク#	保持時間	面積%
1	13.955	5.084
2	18.096	94.916
合計		100.000